

Air Pollution Method: A new method based on ionic liquid passed on mesoporous silica nanoparticles for removal of manganese dust in the workplace air

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ABSTRACT

Chronic effect of manganese exposure to humans caused the dysfunction of nervous system. An applied sorbent based on hydrophobic ionic liquid passed on mesoporous silica nanoparticles (IL/MSNPs) was used for adsorption/removal of manganese dust (Mn) from workplace air by solid phase adsorption method (SPAM). In bench scale set up, 5 mL of standard solution of nitrate and oxide of Mn ($0.2\text{--}5\text{ mg L}^{-1}$) was used for generation of manganese dust in pure air by drying procedure, and then was passed through column of IL/MSNPs by SKC pump with flow rate of $200\text{--}500\text{ mL min}^{-1}$ by SKC pump. Moreover, Mn particles were become absorbed/removal from artificial air by IL/ MSNPs at $80\text{ }^{\circ}\text{C}$. The Mn particles separated from column of IL/MSNPs by irrigation of nitric acid solution (2 mL of 0.3 M) before determined by F-AAS/ET-AAS. In optimized conditions, the adsorption capacity of MSNPs and IL/MSNPs for Mn removal from air in batch system (1 Li) was obtained 118.5 mg g^{-1} and 216.2 mg g^{-1} respectively. Ultimately, for validation, spike of Mn particles (bag 1 Li) and ICP was used for dynamic system.

1. Introduction

Environmental pollution by heavy metals has become a serious problem in the world. The mobilization of heavy metals by man through extraction from ores and processing for different applications has led to the release of these elements into the environment. The problem of heavy metals' pollution is becoming more and more serious with increasing industrialization and disturbance of natural biogeochemical cycles. Unlike organic

substances, heavy metals are essentially non-biodegradable and therefore accumulate in the environment. This contamination poses a risk to environmental and human health. Some heavy metals are carcinogenic, mutagenic, teratogenic and endocrine disruptors while others cause neurological and behavioral changes especially in children. Thus remediation of heavy metal pollution deserves due attention. Different physical and chemical methods used for this purpose. Heavy metals enter the environment from natural and anthropogenic sources [1]. The most significant natural sources are weathering of minerals, erosion and volcanic activity while anthropogenic

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sources include mining, smelting, electroplating, use of pesticides, and (phosphate) fertilizers as well as bio-solids in agriculture, sludge dumping, industrial discharge, atmospheric deposition etc. [2]. Examples of essential heavy metals are Fe, Mn, Cu, Zn, and Ni [3,4]. Non-essential heavy metals are those, which are not needed by living organisms for any physiological and biochemical functions. Examples of nonessential heavy metals are Cd, Pb, As, Hg, and Cr [5,6]. Blood, urine, and hair are the most accessible tissues in which to measure an exposure or dose; they are sometimes referred to as indicator tissues. Blood and urine concentrations usually reflect recent exposure and correlate best with acute effects. In addition, air might be useful in assessing variations in exposure to metals over the long term. Manganese is one of the essential metals for the body. Also, this metal (Mn) is a required element and a metabolic byproduct of the contrast agent mangafodipirtrisodium (MnDPDP) [7]. In addition, exposure to manganese in the workplace is an occupational health concern, it is known that even at relatively low levels of exposure subtle neurological effects have been observed in workers [8]. Manganese is a transitional metal and can exist in 11 oxidation states, from 3^- to 7^+ . The most common valences are 2^+ , 4^+ , and 7^+ . The most common valence in biological systems is 2^+ ; moreover, the valence of 4^+ is present as MnO_2 . Mn^{+3} is also important in biological systems. Cycling between Mn^{+2} and Mn^{+3} may be potentially deleterious to biological systems because it can involve the generation of free radicals. Manganese is an essential element and is a cofactor for a number of enzymatic reactions, particularly those involved in phosphorylation, cholesterol, and fatty acids synthesis. Manganese is present in all living organisms [9,10]. The industrial use of manganese has also expanded in recent years as a ferroalloy in the iron industry and as a component of alloys used in welding [11]. Manganese welding is one of the industries exposed to high concentrations of manganese. In this process, manganese metal fumes are produced. According to the NIOSH standard, the exposure limit for this metal is 0.2 mg

m^{-3} [12]. The most common form of manganese toxicity is the result of chronic inhalation of airborne manganese in mines, steel mills, and some chemical industries [10]. Industrial toxicity from inhalation exposure, generally to manganese dioxide in mining or manufacturing, is of two types: The first, manganese pneumonitis, is the result of acute exposure. Men working in plants with high concentrations of manganese dust show an incidence of respiratory disease 30 times greater than normal. Pathologic changes include epithelial necrosis followed by mononuclear proliferation. Mn toxicity has been reported through occupational (e.g. welder) and dietary overexposure and is evidenced primarily in the central nervous system, although lung, cardiac, liver, reproductive, and fetal toxicity have been noted. Mn neurotoxicity results from an accumulation of the metal in brain tissue and results in a progressive disorder of the extrapyramidal system which is similar to Parkinson's disease. In order for Mn to distribute from blood into brain tissue, it must cross either the blood-brain barrier (BBB) or the blood-cerebrospinal fluid barrier (BCB). Brain import, with no evidence of export, would lead to brain Mn accumulation and neurotoxicity [13,14]. At the present time, the most commonly used methods for assessing workplace airborne metal exposures involve collecting air samples on filters and sending them to a fixed-site laboratory where a variety of analytical methods are used. The National Institute for Occupational Safety and Health (NIOSH) has developed one quantitative field-portable methods to measure airborne lead: NIOSH Method 7300, which uses inductively coupled argon plasma, atomic emission spectroscopy (ICP-AES) [15, 16]. Also, many analytical techniques have been employed for the determination of trace levels of lead in real samples such as, high performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS)[17], Inductively coupled plasma mass spectrometry (ICP-MS)[18], inductively coupled plasma atomic emission spectroscopy (ICP-AES)[19], flame atomic absorption spectroscopy (F-AAS) [20],

electrothermal atomic absorption spectrometry (ET-AAS)[21], etc. Nowadays, considerable novel method has been introduced in solid-phase extraction (SPE) by applying new nanomaterials with remarkable physicochemical properties that improve the extraction of analytes. Thus, many carbonaceous materials such as activated carbons[22], carbon nanotubes[23], carbon nanohorns [24], carbon nanocones/disks [25] and graphene [26- 28] have been applied for analytical preconcentration due to their unique properties, such as reduced particle size, big surface area, high adsorption capacity and good chemical stability [29]. Porous solids are used technically as adsorbents catalysts and catalyst supports owing to their high surface areas. According to the IUPAC definition [30]. Larger pores are present in porous glasses and porous gels which were known as mesoporous materials at the time of the discovery of MCM-41. With MCM (Mobil Composition of Matter) 41 the first mesoporous solid was synthesized that showed a regularly ordered pore arrangement and a very narrow pore-size distribution. After the discovery of MCM-41 in 1992. This material has a highly ordered mesoporous hexagonal structure with mesopore diameters varying from 5 to 30 nm porous materials are divided into three classes: pore-size distributions. Other mesoporous solids microporous (<2 nm), mesoporous (2-50 nm) and were synthesized via intercalation of layered mate macroporous (>50 nm). The pore size and the thickness of the silica walls can be adjusted by varying the heating temperature and time in the reaction solution [31]. Careful investigation of structure of SBA-15 showed that material has certain amount of micropores which connect neighboring mesopores [32,33]. The threshold limit values, permissible exposure limit and occupational exposure limits (TLV/ PEL/OEL) of manganese particles exposure in air determined by international organizations such as, occupational safety and health administration (OSHA, PEL), national institute of occupational safety and health (NIOSH, OEL) and American conference of governmental industrial hygienists (ACGIH, TLV)

and were 5mg m^{-3} , 3mg m^{-3} , 5mg m^{-3} respectively [34].

So, adsorption/ removal of manganese particles from work place air has more important, due to the high toxicity in human body. In this study, IL/ MSNPs and MSNPs were used for adsorption/ removal of manganese dust (Mn) from workplace air by SPAM. The flow rate, mass / type of sorbent, temperature, and length column are important parameters which have more effected on removal efficiency of MSNPs from workplace and artificial air. The mean of relative standard deviation and preconcentration factor was less than 5% and 2.5, respectively.

2. Experimental procedure

2.1. Reagents and instrumental

Determination of manganese was performed with a spectra GBC flame or electro-thermal atomic absorption spectrometer (Model, Plus 932, Aus). A Mn hollow cathode lamp operating at a current of 5 mA and a wavelength of 279.5 nm with a spectral bandwidth of 0.2 nm was used. The GBC demountable torch of inductively coupled plasma optical emission spectrometer (ICP-OES, Integra XL, GBC, Aus) with efficient and high performance at reduced gas flow was used for manganese determination. The innovative bayonet mount torch design requires absolutely no re-alignment when replacing individual components. The Integra's standard set of sample introduction components offer unique capabilities that overcome traditional limitations. Optical detector based on dual photomultiplier system (R7154 solar blind tube) with UV detection was used. The plasma gas with 10 L min^{-1} (Ar), auxiliary gas with 0.5 L min^{-1} (Ar), and nebulizer gas with 0.5 L min^{-1} (Ar) were used. The instrumental conditions are shown in Table 1. All reagents with analytical grade were purchased from Merck/Sigma (Darmstadt, Germany). Mn (II) and Mn (V) were prepared by dissolving appropriate amounts of $\text{Mn}(\text{NO}_3)_2$, MnO , and KMnO_4 in DW. The experimental and working standard solutions were prepared daily by diluting the stock solutions with DW. Deionized water

prepared by water purification system (Millipore, Bedford, MA, USA). Cetyltrimethyl ammonium bromide (CTAB), Na_2SiO_3 (28 wt % SiO_2 , 8 wt % Na_2O , 64 wt % H_2O), silica gel, $\text{C}_2\text{H}_5\text{OH}$, NaOH , HCl and HNO_3 all were purchased from Merck, Germany. All chemicals such as HNO_3 and NaOH , acetone were used as purchased and no further purification was performed.

2.2. Synthesis

For synthesis, 3.13 grams of CTAB was added to 70.6 g of DW and stirred to change clear. First, 7.8 g of ethanol was added to the surfactant solution and then, 9.7 g of sodium silicate (28 wt.% SiO_2 , 5 wt.% Na_2O , 65 wt.% H_2O) was mixed to surfactant solution (white suspension). Second, 24.6 g of sodium carboxyl methyl cellulose solution (12 wt.%) was added to the suspension and stirred for 3 h followed by 2 days aging in oven at 70 °C. Then, the precipitate of MSNPS was filtered, washed with deionized water and dried at 100°C overnight. The MSNPS was placed in a furnace and calcined with a heating rate of 1 K min⁻¹ to 550°C and held at this temperature for 6 hours in air. Then, hydrophobic ionic liquid (HIL) of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) passed on mesoporous silica nanoparticles (IL/MSNPs). In addition, 0.4 g of the [BMIM][PF₆] with 3 mL of acetone mixed with 20 mg of MSNPS and after shaking for 3 min, drying up to 75 °C. MSNPs modified with IL was made for further study.

2.3. Procedure

The dust of Mn nitrate and oxide in pure air was

Table 1. Instrumental Conditions for Mn determination by ICP-OES and F-AAS.

	ICP-OES	F-AAS
Element	Mn	Mn
Wavelength (nm)	279.48	279.5
Lamp current (mA)	--	5.0
Slit (nm)	---	0.2
Volume spray injection	0.2 µL per min	2 mL
LOD (µg mL ⁻¹)	0.1	0.33
Range ^a (µg mL ⁻¹)	0.5-10	1—4
Mode	Peak area	Peak area

prepared and simulated in beach scale set up by standard solution of Mn (Fig. 1). The Mn nitrate and oxide was generated from 5 mL of standard solution (0.1 – 5 mg L⁻¹) after drying up to 110 °C by which was mixed with pure air (210 mL of O_2/L ; 2.5 mL of $\text{H}_2\text{O}/\text{L}$) at 25 °C. This mixture was moved to column which was filled with 20 mg of IL/MSNPs, MSNPs and IL by flow rate of 450 mL min⁻¹. After adsorption Mn dusts on sorbent, the column irrigated with 2 mL of nitric acid (0.3 M) and concentration of Mn in final solution determined by F-AAS and ICP-OES. Note, the IL paste on MSNPs caused to increase the adsorption capacity of Mn dust from air as compared to MSNPs. By increasing temperature from 38–70°C, the removal efficiency was almost increased. The removal efficiency of proposed method was calculated by ratio of concentration of Mn in bulk of pilot to concentration of Mn which was determined by ICP-OES/F-AAS. For validation of methodology, different concentration of Mn was generated by pilot and spike to air samples dust. The recovery and adsorption capacity (mg g⁻¹) was calculated at 50°C as follows: C_s and C_b (µg mL⁻¹ or mg L⁻¹) are concentration in sample and blank solution respectively. C_i and C_f are the initial and final concentrations of $\text{MnO}/\text{Mn}(\text{NO}_3)_2$. In addition, the V (mL) and m (mg) were the volume solution and mass of sorbent, respectively. The recovery was calculated by using Equation 2.

$$\text{Eq. 1} \quad \text{Adsorption capacity (mg g}^{-1}\text{)} = [(C_i - C_f) V] / m$$

$$\text{Eq. 2} \quad \text{Recovery\%} = \frac{(C_i - C_f)}{C} \times 100$$

2.4. Characterizations

X-ray diffraction (XRD) patterns were reported by a GBC diffractometer with Be-filtered Cu K α radiation (1.54 Å) operating at 36.5 kV and 30 mA. Diffraction data was recorded between 1 and 10° 2 θ with a resolution of 0.01° 2 θ with the scan rate of 0.520 min⁻¹. Scanning electron micrograph was recorded using a Zeiss DSM 962 (Zeiss, Oberkochen, Germany). The sample was deposited

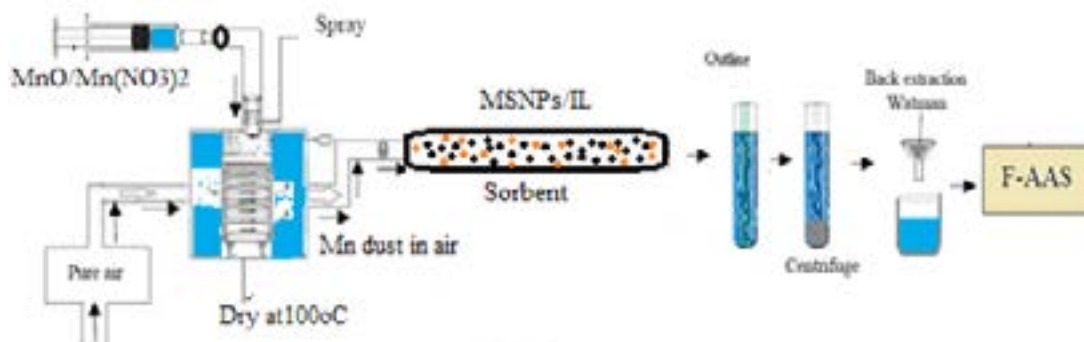


Fig. 1. Beach scale set up with standard solution of Mn by SPAM.

on a sample holder with an adhesive carbon foil and sputtered with gold. Adsorption/desorption of Nitrogen was carried out at 77 K using a BELSORP-mini porosimeter. Prior to analysis the samples were outgassed in-vacuo for 5 hours at 280 °C until a stable vacuum of 0.12 Pa was reached. The pore size distribution was calculated from the desorption branches of isotherms using the standard BJH procedure and also with geometrical (pressure independent) method. Transmission electron microscopy (TEM) was performed on a LEO Zeiss 912 AB. The morphology of MSNPs was examined using scanning electron microscopy (SEM) by Phillips, PW3710, Netherland Company. Sample were dispersed in ethanol and sonicated for 30 minutes and deposited on a copper grid. The synthesis was prepared as the weight of calcined solid per grams of SiO₂ in the initial mixture. The elemental analyzer (CHNS/O, PerkinElmer, 2400

Series II) was used for determination of elemental composition of samples. CHN instrument perform elemental ratio calculations of H/C, N/C, S/C or C/N.

3. Results and discussion

3.1. SEM and TEM imaging

As shown in Figure 2, IL/MSNPs have a highly porous morphology and the mesoporous silica particles are in nanometer range (40-60 nm). Moreover, IL passed on MSNPs did not led to bulky silica nanoparticles. TEM image also illustrates pore structure of IL/MSNPs was shown in figure 5. Based on TEM, the mesoporous are clearly visible in the silica nanoparticles and particle size of the samples is in nanometer range as those observed in SEM image.

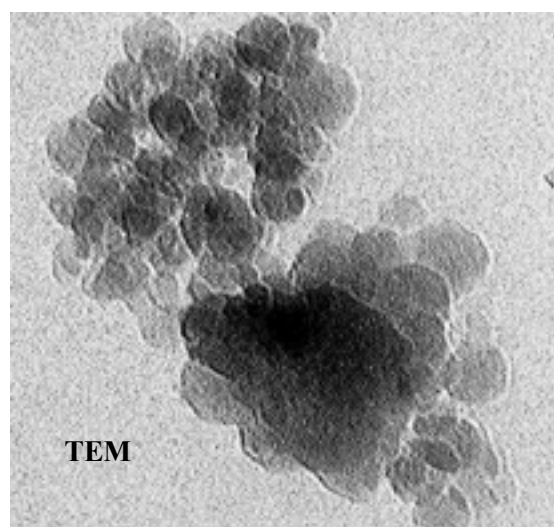
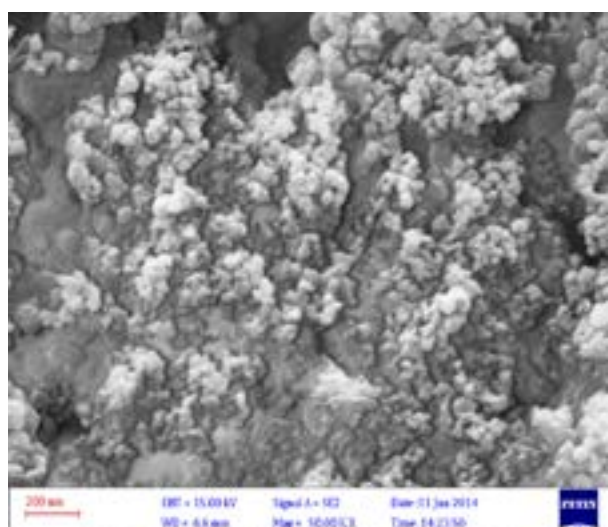


Fig. 2. TEM and SEM of IL/MSNPs sorbent

3.2. Effect of the Mass of MSNPs/IL

The removal efficiency of Mn particles from air with IL/MSNPs was examined between 5-50 mg. The results showed, 15 mg of sorbent had more efficiency for Mn dust removal from air (more than 95%). So, 20 mg of IL/MSNPs was selected as the optimum amounts of adsorbent in gas phase by proposed method. Based on results, 20 mg [BMIM][PF₆] and [EMIM][PF₆] and [HMIM][PF₆] can be removal Mn dust from air up to 38.4%, 26%, and 32%, respectively. So, [BMIM][PF₆] was used as IL in this research.

3.3. Removal efficiency and Adsorption capacity

In this study, the parameters effected on removal efficiency and adsorption capacity were studied by different temperatures (20 – 100°C), flow rates (50, 100, 200, 400 and 600 mL min⁻¹) and initial concentrations of 0.1-5 mg L⁻¹ (ppm). Finally, the adsorption capacity of 216.2 mg g⁻¹, 118.5 mg g⁻¹ and 67.4 mg g⁻¹ was obtained for Mn dust removal from air with 20 mg IL/MSNPs, MSNPs and IL, respectively. Different ILs such as [BMIM][PF₆] and [EMIM][PF₆] and [HMIM][PF₆] passed on MSNPs and effect of temperature on Mn adsorption process was investigated. The results showed, increasing of temperature between 38-70 °C, decreased the viscosity of ILs and caused to efficient removal of Mn dust from air, so, 50°C was selected as optimum temperature. Initial concentrations of

0.01-1 mg L⁻¹ (ppm) of Mn dust were examined by proposed procedure. It seems that, the initial concentrations of Mn dusts depended on mass of sorbent/IL and adsorption capacity. When the adsorption capacity of IL/MSNPs was increased, the more concentration of Mn can be used. As a 20 mg of sorbent and adsorption capacity of 216 mg g⁻¹, the maximum concentration of 4.32 mg of Mn was obtained.

3.4. Effect of air flow rate

By SPAM procedure, the effect of flow rate for Mn dust removal from air was studied for 30 samples. The effect of different flow rates for 20 mg IL/MSNPs, MSNPs, and IL between 50 to 800 mL min⁻¹ was tested at room temperature and 50°C. The flow rate was measured in output of solid phase by a rotameter. The removal efficiency and adsorption capacity of IL/MSNPs, MSNPs and IL for Mn dust were obtained less than 500 mL min⁻¹. So, 450 mL min⁻¹ was selected as optimum flow rate with IL/MSNPs phase for removal of Mn dust from air (Fig. 4).

3.5. Method Validation and Column Condition

The back extraction of Mn from IL/MSNPs was occurred with the minimal concentration of different acid solution. By SPAM method, the different acid solution was used for back extraction Mn ions from column. Reducing pH, leads to dissociation and

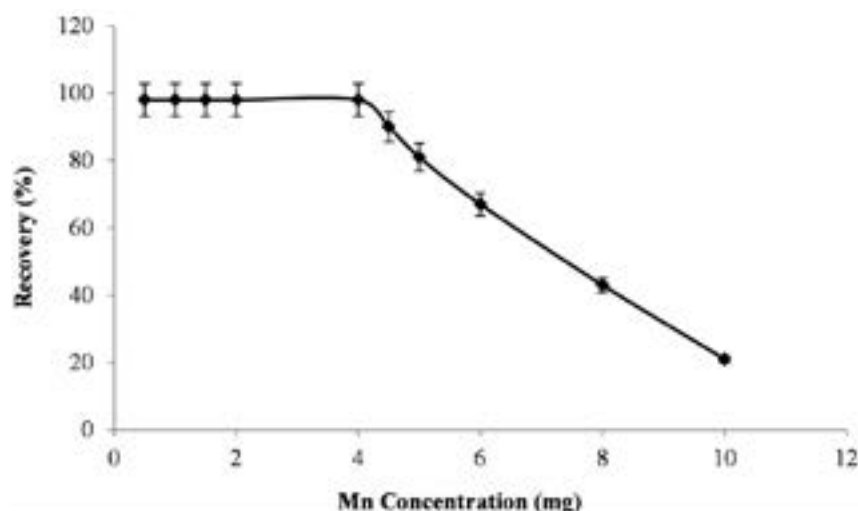


Fig. 2. The effect of concentration for manganese removal from air.

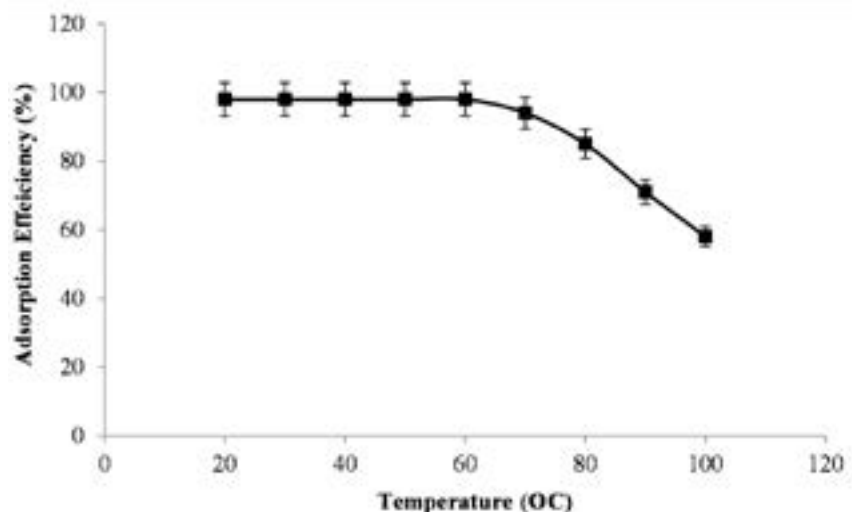


Fig. 3. The effect of temperature for manganese removal from air.

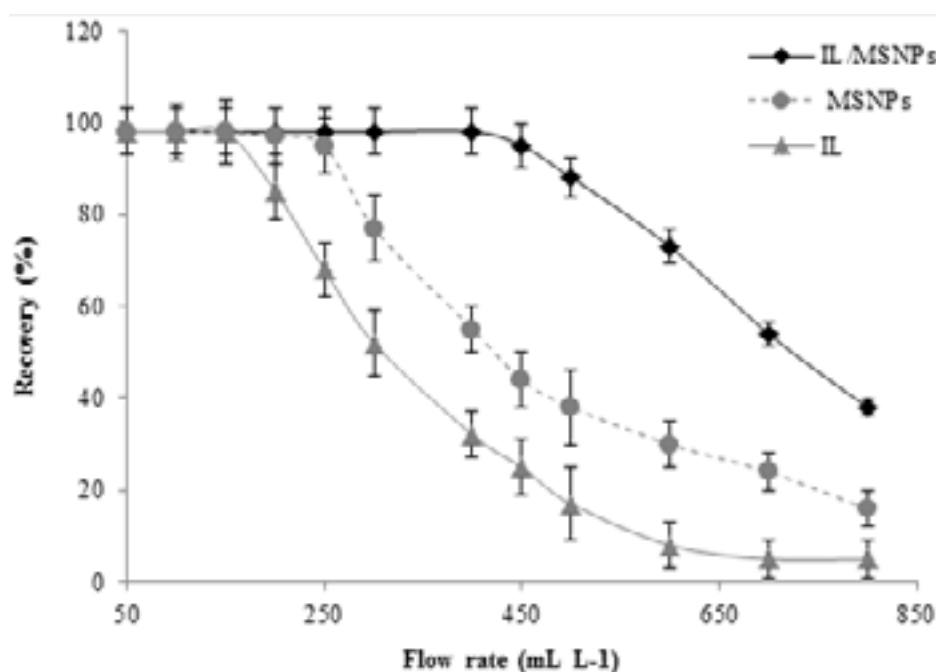


Fig. 4. Effect of flow rate on recovery percentage.

releasing of Mn (II) ions from IL/MSNPs, MSNPs and IL into acid phase. In order to determine the type and amount of mineral acidic solution for lead desorption from IL/MSNPs, different mineral acids such as HCl, HNO₃ and H₂SO₄ (0.1-1 mol L⁻¹) were studied by proposed procedure. The results showed, the 0.3 mol L⁻¹ of HNO₃ solution was selected as a quantitatively acid solution for back extraction of Mn(II) from IL/MSNPs. By experimental design, the interaction between manganese dust in air and IL/MSNPs as a sorbent was evaluated when

the pilot set up correctly. In this method, the IL/MSNPs, MSNPs and IL was used for removal of for Mn dust (MnO and Mn(NO₃)₂) from air by SPAM. For calculating of accuracy and precision of dynamic system, the initial Mn concentration in bench scale set up (bulk container) was determined by F-AAS and compared to proposed method by sorbents. By proposed method, the Mn dust with different concentration from 0.1-1 mg L⁻¹ was generated and passed through dynamic system with 450 mL min⁻¹ and removal from air by 20

mg of IL/MSNPs. The different concentration of standard of MnO and $\text{Mn}(\text{NO}_3)_2$ in air bags and bulk container was determined by F-AAS before used by proposed method. Since standard reference material (SRM) for Mn nitrate and oxide in air dust are not currently available, the spiked of Mn concentration in air which was generated by bench set up ($0.1\text{--}5\text{ mg L}^{-1}$, 450 mL min^{-1}) were prepared to demonstrate the reliability of the method by IL/MSNPs, MSNPs and IL sorbents (Table 2, 3). For determination of manganese concentration in lower and upper linear range, the sample was preconcentration and dilution up to 2.5 and 12.5, respectively. At optimized set up, more than 98% of Mn oxide and nitrate in air dust were removed by IL/MSNPs at 50°C . The high recovery of spiked samples is satisfactorily reasonable and was confirmed using addition method, which indicates the capability of SPAM method for removal of Mn dust from air. After irrigation of column with 2 mL of nitric acid (0.3 M, $\text{pH}<4$), the Mn ions was

back extracted from IL/MSNPs as a solid phase and Mn concentration determined by F-AAS. The validation of methodology was confirmed using power instrumental analyzer ICP (Table 4).

4. Conclusions

In this research, the adsorption/removal of pollutant Mn dust from air was achieved based on IL/MSNPs and MSNPs by SPAM. The results showed, the unique, efficient, and applied procedure which was used for removal of Mn particles dust from workplace and artificial air. For increasing of removal recovery, Mn concentration, amount of IL/MSNPs, temperature from $20\text{--}100$ and flow rate were studied and optimized. The capacity adsorption, recovery, removal efficiency of sorbents was investigated and compared together by F-AAS and ICP-OES. Based on the results, the adsorption capacity IL/MSNPs were more than MSNPs for nitrate/oxide of Mn dust from workplace air. In addition, the efficiency of adsorption for MnO

Table 2. Method validation for IL/MSNPs by spike of Mn oxide in dust air with F-AAS (mg L^{-1})

Bench (Conc.)	Bulk Bench (Conc.)	Added to bench (Conc.)	Found ^a	Recovery (%)
^b 0.2	0.16 ± 0.02	0.2	0.31 ± 0.03	96.8
^b 0.3	0.28 ± 0.02	0.3	0.53 ± 0.05	94.6
^b 0.5	0.44 ± 0.04	0.5	0.87 ± 0.07	98.9
1.0	0.95 ± 0.08	1.0	1.85 ± 0.11	97.3
^c 3.0	2.78 ± 0.16	3.0	5.62 ± 0.27	101.2
^c 5.0	4.69 ± 0.24	5.0	9.02 ± 0.48	96.1

^a Mean of three determinations $\pm$ confidence interval ($P = 0.95$, $n = 5$)

^b (Preconcentration Factor=2.5, Injection volume=2 mL, 450 mL min^{-1} air flow rate, Peak Area, 20 mg, $T=50^\circ\text{C}$, $\text{pH}<4$)

^c (Dilution Factor=2.5, Injection volume=12.5 mL, 450 mL min^{-1} air flow rate, Peak Area, 20 mg, $T=50^\circ\text{C}$, $\text{pH}<4$)

Table 3. Method validation for IL/MSNPs by spike of Mn nitrate in dust air with F-AAS (mg L^{-1})

Bench (Conc.)	Bulk Bench (Conc.)	Added to bench (Conc.)	Found ^a	Recovery (%)
^b 0.4	0.35 ± 0.02	0.4	0.67 ± 0.04	95.7
^b 0.6	0.52 ± 0.05	0.6	0.99 ± 0.10	95.2
1.0	0.92 ± 0.09	1.0	1.88 ± 0.12	102.3
2.0	1.86 ± 0.13	2.0	3.65 ± 0.18	98.1
^c 3.0	2.65 ± 0.17	3.0	5.18 ± 0.28	97.7
^c 5.0	4.51 ± 0.25	5.0	8.94 ± 0.48	99.1

^a Mean of three determinations $\pm$ confidence interval ($P = 0.95$, $n = 5$)

^b (Preconcentration Factor=2.5, Injection volume=2 mL, 450 mL min^{-1} air flow rate, Peak Area, 20 mg, $T=50^\circ\text{C}$, $\text{pH}<4$)

^c (Dilution Factor=2.5, Injection volume=12.5 mL, 450 mL min^{-1} air flow rate, Peak Area, 20 mg, $T=50^\circ\text{C}$, $\text{pH}<4$)

Table 4. Comparing of different sorbents for removal of Mn oxide by ICP-OES/F-AAS (mg L⁻¹)

Sample*	Bulk Bench (Conc.)	Added (Conc.)	F-AAS ^a (Conc.)	ICP-OES ^a (Conc.)	FAAS Recovery (%)	ICP-OES Recovery (%)
IL	1.0	-----	0.26± 0.02	0.29± 0.02	26	29
		1.0	0.54± 0.03	0.56± 0.04	28	27
		2.0	0.83± 0.04	0.88± 0.05	28.5	29.5
IL/MSNPs	1.0	-----	0.98± 0.05	0.99± 0.06	98	99
		1.0	1.99± 0.09	1.97± 0.10	101	98
		2.0	2.96± 0.15	2.95± 0.16	99	98
MSNPs	1.0	-----	0.52± 0.03	0.56± 0.02	52	56
		1.0	1.03± 0.05	1.11± 0.06	51	55
		2.0	1.49± 0.07	1.64± 0.08	48.5	54

^a Mean of three determinations ± confidence interval (P = 0.95, n = 5)

* (450 mL min⁻¹ air flow rate, Peak Area, 20 mg, T=50°C, pH<4)

and Mn (NO₃)₂ was increased at more than 38-70 °C and decreased more than 90 °C. Finally, the results showed that the flow rate is important factor in dynamic system, and optimized flow rate was achieved less than 450 mL min⁻¹. The method had good ability for removal of Mn dust from air.

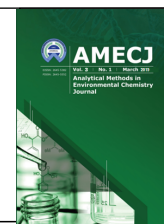
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A review of constructive analytical methods for determining the amount of aluminum in environmental and human biological samples

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ABSTRACT

Aluminum is a toxic metal and cause pollution in soil, water, and air. Afterwards, a lot of patients suffer renal failure due to the accumulation of aluminum in the tissues of kidneys. Also, high concentration of aluminum in plants tissues makes agricultural food toxic. Therefore, measuring aluminum in water, soil, air, human organs, tissues of plants and each food (or agricultural product is so necessary for protecting human healthy. In this paper, the analytical methods which have been applied for measuring the amount of aluminum from 1970 to 2019 are focused on. Also, the effect of some parameters such as pH and temperature on decrease or increase in the amount of aluminum in water and other samples are stated. Ultimately, it is worthwhile to mention the analytical methods which are more time-consuming, cost-effective, applicable, and precise for determining the amount of aluminum now. In this review, the analytical methods such as fluorimetric, ICP-MS, colorimetric, graphite furnace/flame atomic absorption spectrometry, etc. which have been applied for measuring the amount of aluminum (especially Al^{+3}) in environmental and human biological samples are assessed.

Keywords:

Analytical and Bioanalytical methods
Aluminum
Human and Environment samples
Toxicity and Measuring.

1. Introduction

Aluminum is a toxic metal. This toxic metal has polluted a lot of water wells, springs, lakes, groundwater aquifers, rivers, and soil in most parts of the world. Unfortunately, aluminum accumulates in plants' tissues. Also, aluminum foils during a little time penetrated into food. Nowadays, a lot of patients who have suffered chronic renal failure in the world were evaluated. People are living next to the mines are exposed to this toxic

metal. In addition, aluminum which conveys to our bodies by having agricultural products and drinking water accumulates in the tissues of organs, and after a little time, their functions are suppressed. Also, a lot of analytical methods such as weight loss measurements, environmental scanning electron microscopy, electro-thermal atomic absorption spectrometry, colorimetric, kinetic fluorimetric, chelation, and inductively coupled plasma-mass spectrometry have been presented by a lot of researchers in the world for determining the amount of aluminum especially Al^{3+} in water, soil, and biological samples. World

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health organization (WHO) has studied a lot on the amount of allowed aluminum in every organ of our body [1-5]. Wong et al reported about aluminum and fluoride contents of tea, with emphasis on brick tea and their health implications [1]. Mameri et al showed that defluoridation of water by small plant electrocoagulation using bipolar aluminum electrodes can be separated many pollutions from matrix but can be caused aluminum pollutions in environment [2]. Aluminum and heavy metal contamination of ground water was evaluated and determined by Momodu et al. by ET-AAS [3] and Havas et al. reported analytical method based on aluminum bioaccumulation in soft water at low pH [4]. Shaw et al. showed the effect of aluminum in the central nervous system (CNS) which have caused to toxicity in humans and animals [5] and Brown et al. research in analytical method in aluminum species at mineral surfaces by instrumental analysis [6]. In 1995 -1996, Hodson et al and Neuville et al used different methods based on for measuring Al in plants and glasses which was effect in environment and humans [7,8]. Krewski et al showed Human health risk assessment for aluminium, aluminium oxide, and aluminium hydroxide in humans in 2007 [9] and uptake of fluoride, aluminum and molybdenum by some vegetables from irrigation water was studied by Khandare et al. at 2006[10]. Occasionally, aluminum was used in different industry with variety of method which was hazard effect in humans and environment. For examples, in 2003, Zn/Al hydrotalcite-like compound (HTlc) was used for removal of fluoride from aqueous solution by Das et al [11]. Cosby et al used a modeling the effects of acid deposition for extraction of aluminum and Assessment of a lumped parameter model of soil water and stream water [12]. Human exposure to aluminum was evaluated by Niu and Exley [13-15]. Dunemann et al., showed, simultaneous determination of Hg (II) and alkylated Hg, Pb, Al and Sn species in human body fluids using SPME-GC/MS-MS [16]. Messerschmidt et al used adsorptive voltammetry procedure for the determination of platinum and aluminum baseline levels in human body fluids

[16] and release of metal ions from dental implant materials was shown through determination of Al, Co, Cr, Mo, Ni, V, and Ti in organ tissue by Lugowski et al [17]. Also, a review paper about determination of metal-binding proteins by liquid chromatography was reported by journal of Analytical and bioanalytical chemistry in 2002 [18]. The concentration of other metals in human body was evaluated based on different analytical methods by GC-MS, SPME-CGC-ICPMS, GC-MIP-AED, and anodic stripping voltammetry [19-26]. Khanhuathon et al used a spectrophotometric method for determination of aluminum content in water and beverage samples employing flow-batch sequential injection system at 2015 [27]. Liu et al applied Determination of metals in solid samples by complexation/supercritical fluid extraction based on gas chromatography and atomic emission detection for determination metals [28]. Other methods such as, fluorescence detection and film microelectrode based on voltammetry was used for determination metals in body fluids was used [28-31]. The speciation of aluminum in human serum was done by Sanz-Medel et al in coordination chemistry reviews [32]. In 2017, the Nano analysis in biochemistry for separation of aluminum in blood of dialysis patients has been developed with graphene oxide Nanoparticles which have been dispersed in Ionic Liquid [33].

Moshtaghi et al showed a method for aluminum determination in serum of dialysis patients by F-AAS [34]. Halls [35], Bettinelli [36], and Narin [37] have determined the amount of aluminum in dialysate fluids and environmental samples by ET-AAS [34-36]. Aluminum in biological fluids and dialysis patients was determined with 8-hydroxyquinoline/ extraction/fluorimetry by Buratti [38] and Davis et al showed a method for determination of aluminum in human bone [39]. Also, aluminum in biological and water samples based on cloud point extraction /furnace atomic absorption spectrometry was developed by Sang in 2008 [40]. Selvi et al introduce a method analysis for determination of Aluminum in dialysis patients by Atomic Absorption Spectrometry by

Coprecipitation with LaPO_3 in 2017 [41]. Many methods for determination of aluminum was done such as lubricating oils emulsified in a sequential injection analysis system, tri-calcium Phosphate (TCP), eriochrome cyanine with CPE, dopamine as an electroactive ligand, by ET-AAS/F-AAS from 2002 to 2016 [41-45]. The risk assessment of aluminum based on determination of aluminum in food/meat was developed by Bassioni and Juhaiman in 2012 and 2015 respectively [46,47]. Novel method for determination aluminum in human brain tissue using lumogallion /fluorescence microscopy was obtained by Mirza in 2016 [48]. Sorenson et al. showed that aluminum in the environment and human samples can be evaluated and Rana Sonia used Schiff base modified screen printed electrode for selective determination of Al^{3+} in different matrix in 2017 [49,50]. Determination of aluminum with deep eutectic solvent/microextraction method was developed in water and food samples in 2018 by Panhwar et al [51] and Lia-yan Liu used by ICP-AES [52]. Zuziak et al., applied a voltammetry for determination of aluminum in 2017 [53]. Chao, Litov and Dórea introduced a analytical method for breast milk samples [54-56]. In addition, many analytical method was used for determination and separation Al from different matrix such as blood and water samples [57-67]. In this research paper, it has been tried that the analytical methods which have been used for quantifying the amount of aluminum in water, soil, and biological samples will be assessed. Also, the assessment helps all scientists and researchers find and use the best analytical approaches which are more precise and accurate for determining the amount of aluminum in the samples. Moreover, this review paper presents the cost-effective and time-consuming methods which have been used since 1970 to 2019.

2. Experimental Procedures

2.1. Methodology

In this section, the analytical methods for measuring aluminum in human body and Environment matrix were studied. The different metals spread on the earth's crust; aluminum (Al) has the third most

abundant element as compared to other metals with percentage of 88% gram per kilogram. The free aluminum has never seen in nature and mostly exists in aluminum silicate minerals and rocks [6-8]. Aluminum is also exist in different matrixes such as; air, soil, water, foods and environment. Based on weathering of metals, the metals enter to waters and human. Human activity by industrial processes, waste water effluents and dust as a major constituent of aluminum compounds can be released in air, waters, vegetables and human [9,10].

Many parameters such as coordination chemistry, pH, and characteristics have effects on behavior of aluminum in environment [11,12]. In addition, by biogeochemical cycle of aluminum, geochemical formations and soil particulates, and air particles change to aqueous environments and then enter to soil or sediment. Aluminum is widely was used as applied metal in all world as a building material. The different forms of aluminum compounds have been made by mixing of other elements. In different pH and conditions, Al can be used with other ions with different valence states. Aluminum is used in many fields such as antacids (Al-Mgs), food additives (Al(OH)_3), skin ointment, cosmetics products, container, and as a metal contaminants appeared in milk products, juice, fish, and tea [13-21]. Aluminum also enters in drinking water due to the water treatment process, weathering rocks and soils and acid raining. Aluminum is used in many industries due to special physical and chemical property. So, aluminum particulates are seriously exposed by workers of aluminum factories. The absorption of aluminum in human body was achieved by many materials such as citrate, Fe in hem, Ca, F, etc. [21-26]. A precise, sensitive and selective spectrophotometric method for determination of Al^{3+} using (ECR) as a chromogenic reagent in the presence of N, N dodecyl trimetylammonium bromide (DTAB) has been developed by Khanhuathon et al in 2015 [27]. Modern spectrophotometric approach for determining Al^{3+} in waters and soft drinks by using eriochrome cyanine R(ECR) has been

presented by Khanhuathon et al. In addition, in their approach, R(ECR) which is a chromogenic reagent has been used in the presence of N, N dodecyl trimethylammonium bromide (DTAB). Their study shows that at 584 nm, a maximum absorption is obtained when pH is equal to 5, Al-ECR complex is used. In the mentioned study, the effects of some parameters such as amount and type of surfactant, pH, and concentration of EOR on the rate of absorption of Al have been assessed. Moreover, after optimizing the condition, a linear range of 0.01 to 0.50 mg L⁻¹ aluminum is received. Also, the range of detection has been 0.0020 mg L⁻¹, and the range of quantification has been 0.0126 mg L⁻¹. Based on their study, the relative standard deviation of their approach has been 13% [28-33]. When the rate of absorption is 0.05 mg L⁻¹, the applicability of their approach for determining Al contents is tested on many water samples and soft drinks. Also, the outcomes of their method are similar to the ICP-AES method. In addition, their methods can recovery up to 80%. In addition, based on their studies, R(ECR) is a suitable reagent for determining the amount of Al in every

kind of water. Moreover, in their approach, some cons of using Al-ECR complexes such as time consuming have been there. In addition, in the mentioned approach, pH and temperature of the complexes must be controlled. Also, in the study, the effects of various surfactants on two properties of the complexation and reagent, i.e. spectra and sensitivity, when the pH is equal to 5 have been considered. The consideration demonstrates the highest sensitivity of the absorption spectrum and maximum wavelength which is equal to 584 nm is obtained. Moreover, DTAB (dodecyl trimethylammonium bromide) is the most effective surfactant for improving the sensitivity of AL-ECR [34-42]. Moreover, the study demonstrates that the maximum absorption is obtained when pH is equal to 5, as seen in the following figure (Figure 1).

Yildiz et al have studied on determining Al for tri-calcium phosphate (TCP) anhydrous powder by flame atomic absorption spectrophotometer in 2016. Based on their study, there is about 350 mg/kg (w/w) of aluminum in tri-calcium phosphate anhydrous powder. In the study, the amount of their metal in the powder is determined using atomic

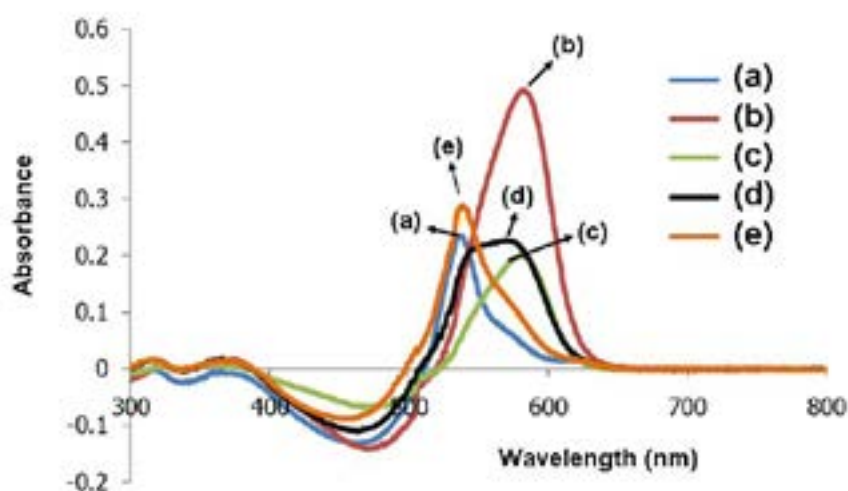


Fig. 1. Spectra of Al-ECR complexes in the absence (a) and in the presence of various surfactants (b) DTAB, (c) CTAB, (d) SDS and (e) Triton X-100. Conditions: 0.2 mg L⁻¹ Al, 0.15 mmol L⁻¹ ECR and 3 mmol L⁻¹ surfactant, pH 5.

absorption spectrophotometer. In their approach, the outcomes of Al which have been obtained by using the $N_2O-C_2A_2$ flame are similar to the previous studies. Also, the standard calibration curve has been done automatically. Moreover, the accuracy of their method has been considered using recovery test of aluminum. Finally, their results show that the amount of Al has been 0.5 mg/kg in the detection limit and there is a suitable linearity based on their analysis [43].

Hejri et al has studies on determining trace aluminum with eriochrome cyanine R after cloud point extraction in 2011. In their study, for determining ultra-trace amounts of Al^{3+} in well waters, the approach of cloud point extraction has been used. In addition, during the study, the surfactant of cetyltrimethylammonium bromid has been used. Based on their study, linearity has been ranged from 0.2 ng mgL^{-1} to 20.0 ng mgL^{-1} . In their study, the limits of detection is about 0.05 ng mgL^{-1} ; moreover, these limits are governed for determining Al^{3+} . In their method, an interaction is there between surfactants and metal-dye complex. Also, in the mentioned method, a ternary complex which involves surfactant monomers is formed. Moreover, the efficiency of their method increases when pH is equal to 5.5. Also, their results show that by increasing and decreasing pH, sensitivity will be reduced [44]. In addition, determining aluminum in biological fluids using an electroactive ligand, dopamine have been studied by Bi et al in 2002. Based on their study, by increasing Al concentration, decreasing trend of the differential pulse voltammetric anodic peak is linear. Also, when the experimental conditions are optimum, two linear ranges which are about 5.0×10^{-8} to $4 \times 10^{-7} \text{ M}$ and 4.0×10^{-7} to $7.2 \times 10^{-6} \text{ M}$ Al^{3+} are gained. They have selected some samples which have been obtained from synthetic renal dialysate, human whole blood, the urine of patients who have suffered diabetes. The amount of Al^{3+} has been measured in the samples using dopamine. Afterwards, they have verified the depression electrochemical activities of DA by making a comparison between electrochemical behaviors

and the spectroscopic responses. In their study, an indirect method for determining Al^{3+} with an electroactive ligand has been applies in biological fluids using differential pulse voltammetric. Finally, in the study, a good and suitable agreement between the results of the study and previous studies have been made [45]. In addition, Will et al have considered two methods for determining Al^{3+} concentrations in blood in 1990. In their study, the amount of Al which causes chronic renal failure in patients have been mentioned. In their first method, plasma samples have been diluted with HNO_3 /triton x-100 matrix four times. Also, in the second method, samples are diluted with an equal volume of $Mg(NO_3)_2$ matrix, moreover their samples have been atomized from a L'vov platform. In addition, analytical recovery of Al which has been added to is about 98%. Also, they performed and tested the samples in sealed containers to maintain them against contaminations. In the first method, a 10-ml sample which is the representative of whole blood has been selected, then centrifuged. Afterwards, the plasma has been washed by using a disposable polyethylene pasteur pipet at 4°C . In their second method, samples have been diluted in de-ionized water with the solution of $Mg(NO_3)_2 \cdot 6H_2O$ which is 5-46 mmol/L. Also, for analyzing the samples, atomic-absorption spectrometric and electrothermal graphite atomizer with the instruments of model 5100-PE and 5100-PC have been used [46]. Bassini et al have studied on the amount of Al which causes that food would be contaminated in 2012. Unfortunately, transferring aluminum from foil to food is hazardous. In their study, three techniques such as weight loss measurements, environmental scanning electron microscopy, and inductively coupled plasma-mass spectrometry have been used for analyzing the samples which have been selected from the foods that exposure to aluminum foil. The outcomes of their studies show that in acidic food and cooked food, the amount of Al is higher in comparison with the other kinds of foods. In addition, based on their results, the leaching of Al from foil into food solution as a solid phase is the same as liquid and vapor phases.

Moreover, by increasing temperature, leaching of Al is increased. Also, when pH decreases, the rate of leaching rises. Moreover, using aluminum foil causes a lot of diseases in human body [47]. Al Juhaiman has studied the cons of aluminum foil which has been wrapped around baking meat in 2015. Although who has reported the negative effect of Al foils, unfortunately, a lot of companies of producing food use it. In their study, the effect of temperature and cooking time on the amount of Al which leaches into the food has been assessed. Based on their results, the leaching of Al in fish has been the highest, and in chicken, the rate of leaching of Al has been the lowest. Also, cooking foods in aluminum pans or other aluminum dishes increase the rate of leaching. In addition, based on corrosion weight equation, the rate of Al leaching in fish, after 60 minutes cooking, is equal to 38.67 mg Al/kg. Also, when this rate is obtained, CR is about $(7.000.71 \pm) \times 10^{-3}$ [48]. In addition, Exley et al have studied on the accumulation of aluminum in brain tissue of human in 2016. Based on the study, when aluminum accumulates in brain tissue, the human will suffer neuro-degenerative diseases which include Alzheimer's disease. Also, a few studies have been done on visualization of aluminum. In this study, for measuring aluminum in brain tissue, transversely heated graphite furnace with atomic absorption spectrometry has been used. In their study, fluorescence microscopy and the flour lumogallion have been developed and validated for showing the presence of aluminum in brain tissue. Their research has shown that fluorescence of aluminum in brain tissue is different with other metals that accumulate in brain tissue. Orange fluorescence shows that there is some aluminum in brain tissue. Their method, i.e. fluorescence microscopy helps physicians to get more information about the amount of Al in brain tissue, and thereby the prevention of being suffered Alzheimer's can be followed. Also, Exley et al have used 4-chloro-3-(2,4 dihydroxyphenylazo)-2-hydroxybenzene-1-sulphonic acid as a lumogallion for measuring the amount of Al^{3+} in brain tissue. Moreover, the lumogallion has been used for

measuring the amount of Al^{3+} in seawater. When it is used in seawater, the limit of detection of CA is equal to 2 Nm. Furthermore, the method of fluorescence has been used for measuring and determining the amount of Al^{3+} in plants. Moreover, during the test of determination of amount of Al^{3+} in the left part of the brain of a patient using fluorescence microscopy and 1Mm lumogallion, pH has been equal to 7.4. based on their results, the concentration of Al^{3+} in the left part of the brain of the patient who has suffered Alzheimer disease ranges from 0.45 $\mu\text{g/g}$ dry wt. (in the hippocampus) to 1.75 $\mu\text{g/g}$ dry wt. (in the occipital lobe). In addition, orange fluorescence indicates that there is some aluminum in each tissue. Also, in their study, it is found out that if pure agarose is spread with Ca^{2+} , Cu^{2+} , Mg^{2+} , Fe^{3+} or Zn^{2+} , no fluorescence related to lumogallion is appeared. Moreover, Exley et al have found out that the rate of replication of aluminum concentration in brain tissue ranges from 0.01 $\mu\text{g/g}$ dry wt. to 5.58 $\mu\text{g/g}$ dry wt. [49]. Moreover, Leng et al have been used chromogenic agent with alizarin reds for determining the amount of trace aluminum in 2015. Moreover, the determination of trace aluminum with the agent has been carried out using ultraviolet spectrophotometer. Also, the effective parameters on the determination such as pH, temperature, and reaction time have been optimized. Their results demonstrate that Fe^{3+} and Cu^{2+} have effects on determining Al^{3+} , while K^{+} and Na^{+} have little influence on the mentioned approach [50-53].

In the procedure, an efficient and new approach based on graphene oxide nanoparticles (GONPs) which have been dispersed in ionic liquid (IL) has been used for in-vitro separation/extraction of trace Al from the blood of dialysis patients by ultrasound assisted-dispersive-micro solid phase extraction (USA-D- μSPE) procedure. Under the conditions which have been optimized, the linear range (LR), limit of detection (LOD), and preconcentration factor (PF) have been obtained 0.1–4.8 $\mu\text{g L}^{-1}$, 0.02 $\mu\text{g L}^{-1}$, and 25 for blood samples respectively (RSD < 5%). The results of blood samples have demonstrated that the aluminum concentration after dialysis has

been higher than before dialysis (128.6 ± 6.7 vs 31.8 ± 1.6 , $P < 0.05$). The mean of blood aluminum has been significantly higher in dialysis patients in comparison with normal control respectively (113.5 ± 7.12 vs 1.2 ± 0.1). The developed approach based on GONPs/IL has been successfully used for extracting critical level aluminum from human blood, and the method is suggested for in-vivo extraction from human body of dialysis patients after being advocated on an appropriate surface with biocompatible materials within the human body. Some other approaches like atomic emission spectrometry preliminary essay to measure the amount of biological materials which have been carried out with existing analytical methods such as spark or flame atomic emission spectrometry 60-63 with sensitivities approximately 300-3000 less than ETAAS29 and before many of the contamination problems associated with sample collection and preparation were fully appreciated. These methods have now been largely abandoned but other sources for atomic emission spectrometry (AES) have proved successful. A constant-temperature graphite furnace and measured aluminum in blood and digested tissues with a detection limit around two- to fourfold better than ETAAS has been developed by Baxter et al. Instrumentation for electrothermal atomization atomic emission spectrometry has to be constructed by the user; however, some commercial inductively coupled plasma atomic emission spectrometry (ICP-AES) systems are available.

Allainss,M-66 has been used ICP-AES for measuring aluminum in serum, water, and dialysis fluids. Although he achieved excellent results, it is the experience of most workers that the sensitivity is insufficient to determine normal concentrations and that time consuming preconcentration steps, with risks of contamination, are necessary. In the other papers, the chemical speciation of aluminum in the low molecular mass (LMM) and high molecular mass (HMM) fractions of human serum has been discussed by Alfredo Sanz-Medel et al [32]. The methodologies, the experimental and instrumental requirements and the ability of the

reported analytical procedures for identification of HMM and LMM aluminium species in human serum are tested in detail. Nonchromatographic separations coupled to electrothermal atomic absorption spectrometry for aluminum detection are compared with chromatographic techniques (size exclusion chromatography, anion exchange chromatography, and fast protein liquid chromatography) coupled to ETAAS or inductively coupled plasma mass spectrometry (ICP-MS) detection for Al-HMM species assessments. As stated before, the complexity of the human serum samples follows a knowledge and judicious choice of different principle based separations assisted by complementary selective detectors. In this vein, a most advisable first step is the fractionation of the aluminum biocompounds into two broad groups: (a) HMM and (b) LMM type of species. This 'primary' or 'rough information' can provide a constructive preliminary information. Thus, by using non-chromatographic approaches, it seems that about 10% of aluminum in human serum is ultrafiltrable [32-41]; therefore, about 90% of aluminum should be bound to non-ultrafiltrable HMM proteins. The query is now which protein(s) binds aluminum in human serum. In order to reply this query, chromatographic approaches coupled to Al^{3+} specific detectors are the most powerful analytical tools. However, at this stage, a new controversy arose on the type of chromatography to be applied: early workers in this field used size exclusion chromatographic approaches for separating human serum proteins [37,38-41]. The total concentration of Al^{3+} in human serum of healthy subjects which has been reported by Mothes et al [24] ranges from 0.5 to 8 mg dm³, while a recent report from the Sanz-Medel's group [32] has indicated even lower normal aluminum concentration (in general below 0.35 mg dm³) [24]. Due to such very low concentrations, the speciation of aluminum in healthy subjects has been possible only in spiked samples. Most of the investigators have used spiked serum in such a way that total serum aluminum, after spiking, ranged between 100 and 200 mg dm³ matching high concentrations which could

be found in the serum of some dialysis patients. Since reported the concentrations of ultra-filterable aluminum in serum represented only 10/ 20% of total aluminum [41], it was necessary to apply very sensitive analytical procedures in order to identify and quantify the LMM-Al complexes present even in spiked serum and in high aluminum level sera of dialysis patients. Nowadays, there is no doubt that the analytical approaches for Al^{3+} speciation in human serum are needed to appropriately address the biomedical problems still waiting for a solution. The vitality of the research work on the development of new analytical methodologies for Al speciation in human serum is obvious from the number of published papers during the last decade. However, it is obvious that the speciation of Al^{3+} in biological fluids has been full of problems with difficulties in the past as is still in a state of development that has to overcome serious problems for its extensive application. Although earlier work seems to have been plugged with serious contamination problems, some sort of consensus on the chemical speciation of serum aluminum has emerged in recent years based on the results of some work carried out first by ultramicrofiltration, which demonstrates that usually 90% of total serum Al^{3+} is not ultra-filterable (i.e. the metal is bound to HMM bio compounds). Speciation of Al^{3+} in human serum is an extremely difficult task because the basal levels of this element in serum are lower than 2 mg/l and these minute amounts are fractioned in the speciation process. For making matters worse, the risk of significant exogenous Al contamination is very high.

In the other study, a reliable determination of aluminum in serum and aqueous solutions has been described by Moshtagi-Iie et al. In this method, using 10% HNO_3 for glassware and 1 mmol EDTA for plastic containers can prevent the problem of contamination since no detectable aluminum has been found by making a comparison between the absorption signals obtained from fresh sera and water samples with those obtained from samples held in the containers (data not shown). The temperature stages used led to the

complete atomization of aluminium and produced a sensitivity and detection limit of 15 pg, and 2.1 mg.L^{-1} respectively. Nameless atomic absorption (Perkin-Elmer 603 spectrophotometer) is used by Parkinson et al. Moreover, a sensitivity and detection limit of 35.5 pg and 2.3 mg.L^{-1} have been presented by them. Our findings are in good agreement with their observations. Obviously, the sensitivity produced by our instrument has been much better due to the atomic absorption model which has been modern. In the present method, the linearity of our calibration curve has been up to 10.60 ng/mL of aluminum. With such a calibration curve, we were able to measure aluminum concentrations in serum, although the serum should be diluted in higher levels of aluminum. Mazzeo Farina and Cerulli has been reported a linearity of up to 50 ng mL^{-1} which has been in agreement with our findings. In the other study, it is found out by Halls et al that aluminum toxicity has been shown to be a problem for patients with renal failure on dialysis, leading, in severe cases, to dialysis dementia, bone disease, and anemias [35]. The measurement of aluminum in dialysate fluid can be used to monitor the exposure of patients on dialysis. The change in the concentration of aluminum in the fluid after dialysis can be used to calculate transfer of aluminum to and from a patient, and to follow the removal of aluminum with the chelating agent, desferrioxamine. Moreover, 5 dialysate fluids can be analyzed by electro-thermal atomic absorption spectrometry with electro-thermal atomization (ETAAS-ETA) in the same way as serum. The object of this work has been to develop a sensitive and accurate method based on ETAAS-ETA, which decline the analysis time in accordance with principles which have been described previously. In the other methods, a modern chelating resin based on poly [4-(1-azo-3-hydroxy-4-(N,N-dicarboxymethyl) aminophenyl) styrene] for determining traces level of aluminum and titanium have been proposed by Basargin et al. For using it in the solid phase extraction of aluminium, a polystyrene-co-divinylbenzene commercial resin (Amberlite XAD-4) has been modified by grafting onto salicylic acid

by Bettinelli et al [36]. Also, a new chelating resin by fictionalisation of polystyrene–divinylbenzene with imidazole 4,5-dicarboxylic acid through N=N bonding for the speciation of vanadium (IV) and vanadium (V) have been synthesized. Deionized water is used for preparing all solutions. Otherwise, stated analytical-grade acids and other chemicals used in this study have been achieved from Merck, Darmstadt, Germany. Stock solutions of all metals, containing 1000 mg^L⁻¹ (Merck) have been used for preparation of the standards for the calibration curve. The calibration standards have never been submitted to the preconcentration procedure.

The XAD-1180-PV column approach has been tested with model solutions prior to the determination of aluminum in the samples. For the metal determinations, 50 ml of solution which contains 0.20 g of Al³⁺ has been added to 10 ml of buffer solution (the desired pH between 2 and 10). The column has been preconditioned by passing buffer solution. The solution has been allowed to flow through the column under gravity at the flow rate of 4 ml min⁻¹. After passing this solution ending, the column has been rinsed with twice 10 ml of water. The adsorbed metals on the column have been eluted with 5–10 ml portion of 2 M HCl. The eluent has been analyzed for determining the concentration of aluminum by graphite furnace atomic absorption spectrometer. The characteristics of XAD-1180-PV chelating resin were prepared. The thermogravimetric analysis curve of the XAD-1180-PV chelating resin is shown in three steps. In the first step, a mass loss of 23% up to 105 °C to be due to adsorbed water on the resin. In the second step, mass loss is 9.0% up to 340.0 °C. In the third step, mass loss is 34.0% up to 458 °C. The mass losses in the second and third steps are similar to pyrocatechol violet. There is an agreement between the situations and the previous studies [24–29]. When the infrared spectra Amberlite XAD-1180 and XAD-1180-PV resins have been compared with each other, there are additional bands at 1720, 1562, 1374, 1195, and 1120 cm⁻¹ which seem to originate due to the modification of resin by the ligand. In addition, there are the characteristics of

C=O, –N=N–, C–OH, –S–O–, and C–N vibrations respectively.

Moreover, determining trace aluminum in biological and water samples by cloud point extraction preconcentration and graphite furnace atomic absorption spectrometry detection have been studied by Hongbo Sang et al. In the practical application of surfactants in analytical chemistry, separation and preconcentration based on cloud point extraction (CPE) are becoming vital. The approach is based on the property of most non-ionic surfactants in aqueous solutions to form micelles and to separate into a surfactant-rich phase of a small volume and a diluted aqueous phase when heated to a temperature known as the cloud point temperature. The small volume of the surfactant-rich phase obtained with this methodology allows us to design the extraction schemes which are simple, cheap, highly efficient, speedy, and lower toxicity to the environment than those extractions that use organic solvents. Cloud point extraction has been used for separating and preconcentrating organic compounds as a step prior to their determination by liquid chromatography and capillary electrophoresis. The phase separation phenomenon has also been used for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes. By research, a TBS-990 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co. Ltd., Beijing, PR China) with a deuterium background correction and a GF990 graphite furnace atomizer system has been used for aluminum determination. An aluminum hollow-cathode lamp has been used as radiation source at 309.3 nm. For CPE, aliquots of 10 mL of a solution containing the analyte, Triton X-114 and PMBP buffered at a suitable pH have been kept in the thermostatic bath maintained at 40 °C for 20 min, and the surfactant-rich phase can settle through the aqueous phase. The phase separation could be occur faster by centrifuging for 5 min at 3000 rpm. After cooling in an ice bath, the surfactant-rich phase became viscous and was retained at the bottom of the tube. The aqueous phases can readily

be discarded simply by inverting the tubes. To decrease the viscosity of the extract and allow its pipetting, 200 L of 0.1 mol L⁻¹ HNO₃ was added to the surfactant-rich phase. 20 L of the diluted extract was introduced into the GFAAS by manual injection. Calibration has been performed against aqueous standards which have been submitted to the same CPE procedure. Ashing and atomization curves have been established using 10 ng mL⁻¹ Al³⁺ solutions which have been sent to CPE procedure and diluted with 10 mL of 0.1 mol L⁻¹ HNO₃. In addition, 20 L of the diluted extract has been used for GFAAS analysis. The ashing and atomization curves of Al³⁺ without CPE procedure were also studied with 10 ng mL⁻¹ Al³⁺ in 0.1 mol L⁻¹ HNO₃. By using CPE procedure, the ashing temperature can be increased by 500 °C over the Al³⁺ solution without using CPE procedure, and the aluminum signal has been enhanced twice. There has been no difference in the shape of the atomization curve for aluminum with and without CPE procedure, only the values of absorbance have been different. In this work, the use of micelle systems as a separation and pre-concentration for aluminum offers some advantages including low cost, safety, preconcentration aluminum with high recoveries and very good extraction efficiency. The surfactant-rich phase can be easily introduced into the graphite furnace after dilution with 0.1 mol L⁻¹ HNO₃, and directly determined by GFAAS. The suggested method can be applied to the determination of trace amount of aluminum in various real samples.

As another method, La³⁺ as releasing agent and ion suppressor in flame for determining metal ions has been used by Kılıçkaya Selvia. LaPO₄ has been used as co-precipitant for separation and pre-concentration of heavy metals in several water samples. Based on our study, LaPO₄ has been firstly used for separation and preconcentration of aluminum in human dialysis samples. This method has several advantages such as low detection limit (LOD), simple, rapid, economic, and precise. The recoveries of aluminum (III) in the presence of the most common matrix elements containing the alkaline and alkaline earth metals were good.

A Perkin-Elmer Analyst A800 Model atomic absorption spectrometer (Northwalk, USA) with nitrous oxide/acetylene flame and a D2 lamp with background corrector was used throughout the determination of Al³⁺ in water solutions and human blood samples. For co-precipitation, 2 µg aluminum (III), 150 µg lanthanum (III), and 150 µL phosphoric acid (1:2 diluted water) have been placed in a centrifuge tube. Then the pH of the solution has been adapted to pH=5 with ammonium acetate/acetic acid, and the solution has been diluted to 50 mL with distilled water. After shaking the solution for several seconds, the solution has been allowed to stand for 15 min and centrifuged at 3500 rpm for 15 min. The supernatant has been removed and the precipitate in the tube was dissolved with 0.1 mL of concentrated HNO₃ and the volume was completed to 2 mL with distilled water. The number of five replicates for each analysis was used. The water/serum/blood samples were determined by flame atomic absorption spectrometry.

3. Results and Discussion

Based on some researches which have been carried out, it is demonstrated that the range of concentrations of aluminum next to industrial companies is about 0.4 to 8.0 µg/m³ [28-42, 50-53]. Moreover, aluminum concentration in drinking water ranges from less than < 0.001 to 1.029 mgL⁻¹ [54]. Moreover, the amount of aluminum of milk of human breast is about 9.2 to 49 µg L⁻¹ [55-57]. The concentration of aluminum of soy-based infant formulas is higher in comparison with milk-based infant formulas or breast milk [57]. Moreover, the rate of Aluminum concentration in finished waters is high due to during the treatment of water, Al³⁺ is added to water [58]. In addition, it had better be mentioned that the amount of Al³⁺ in treated water is three times more than the water which has not been treated. Also, the changes of pH and the humic acid content of the water has effects on the rate of Al³⁺ concentrations which have been dissolved. Also, when pH is less than 5, the concentration of Al³⁺ increases. Unfortunately, aluminum particles have been spread in air, water, and foods, so by

inhaling air and having food and water, the rate of Al^{3+} increases in body tissues [59-62]. Moreover, using other consumer items such as antiperspirants, buffered aspirins, antilulereative medications, and antacids causes an increase in the rate of Al^{3+} in human body. Also, by making a comparison between aluminum which there is in drinking water and food, and medicinal preparations which have Al^{3+} in themselves, the rate of Al^{3+} in medical preparations is much more. The intake or rate of Al^{3+} in food ranges from 3.4 to 9 mg/day [63-65]. The amount of Al^{3+} per tablet/capsule/5 ml dose in many antacids is about 104 to 208 mg [66]. The vegetables and fruit trees which have been grown using treated water has received more Al^{3+} in themselves. It has been found out by Nayak in 2002 that a decrease or increase in Al^{3+} in human body does not have any effects on mortality (or mental health).

People who are living next to the aluminum companies, plants, and mines, as well as other hazardous waste sites will suffer chronic kidney failure. These people or patients must be treated with phosphate binders and long-term dialysis. The infants which have been fed soya, antacids, and antidiarrheal can be exposed to high levels of aluminum. Based on TCRI (Toxic chemical release Inventory), the amount of Aluminum which have been released from 329 aluminum facilities to the environment is about 45.6 million pounds [67]. Moreover, total amount of aluminum oxide which has been released from 59 aluminum processing companies to air, water, and soil is about 2.9 million pounds [67].

Table 2-1 list amounts which have been released from these companies or facilities that they are grouped by state.

The data which have been obtained by TRI are

Table 1. Releases to the Environment from Facilities that Produce, Process, or Use Aluminum Oxide (fibrous forms)

^a Reported amounts released in pounds per year ^b Total release									
State ^c	RF ^d	Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	On-site ^j	Off-site ^k	Off-site
AL	2	0	0	0	0	0	0	0	0
AR	1	0	0	0	0	0	0	0	0
CA	1	0	0	0	0	0	0	0	0
CO	1	0	5	0	480	3	485	3	3
CT	1	0	0	0	0	0	0	0	0
GA	2	16	175	0	3	0	191	3	3
IA	2	0	0	0	40	0	0	40	40
IL	5	76	0	0	122	23	76	145	145
IN	3	901	250	0	5	10	1	10	1
KY	3	243	0	0	27	0	243	27	27
LA	2	0	0	0	0	0	0	0	0
MI	2	0	0	0	375	0	0	375	375

^a The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

^b Data in TRI are maximum amounts released by each facility.

^c Post office state abbreviations are used.

^d Number of reporting facilities.

^e The sum of fugitive and point source releases are included in releases to air by a given facility.

^f Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

^g Class I wells, Class II-V wells, and underground injection.

^h Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other on-site landfills, land treatment, surface impoundments, other land disposal, other landfills.

ⁱ Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

^j The sum of all releases of the chemical to air, land, water, and underground injection wells.

^k Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI05 2007 (Data are from 2005)

not representative of the amount of Al^{3+} in every region due to TRI has selected a few facilities. In addition, inhaling and digesting Al^{3+} exacerbate renal failure, bone disease, and anemia. Moreover, dialysate fluids are made up (in human body) when aluminium which comes from water supplies is consumed or used. Unfortunately, human-mades have changed for ecosystem and increase the amount of aluminium in the environment. The element of Al^{3+} accumulate in plants and water, and thereby all herbivores are exposed to harmful effect of aluminium. Also, when a place is polluted with Al^{3+} , a decrease in the density of populations is occurred.

Emissions of a lot of Al^{3+} into water and soil decreases the fertility. Al^{3+} as a main factor in acid soil can limit crop productivity. The interaction of Al^{3+} with cell walls can cause the disruption of the membrane of plasma, and the disruption or interaction increases when oxidative damage and mitochondrial dysfunction occur. Also, Al^{3+} can damage DNA. When Al^{3+} accumulates in plants tissue, DNA starts to be ruined, and after a little time, it is observed that the rate of the growth of plants is decreased. In addition, all scientist who are study on the effects of environmental change on

the plants are rather hesitant and in a dilemma over whether to adopt the effect of Al^{3+} on the disruption of DNA or not. After carrying out a lot of researches, it has been found out that the accumulation of Al^{3+} in tissue of plants cause that DNA with double strand starts to be broken. In addition aluminum toxicity depends on the acidity of soil and plant resistance. Clinical studies show that the patients who have high concentrations of metals in their brain, bone, and muscle have unexplained syndrome as dialysis dementia. Other researches demonstrated that there are anaemia and ectopic precipitation of calcium in aluminum toxicity syndrome. Here, some effects of aluminum on organ of human body are illustrated, as seen in Figures 2, 3, 4, and 5.

Although by removing dialysis fluid, the rate of Al^{3+} decreases, in the patients who have suffered renal failure, the tissue of their body, especially renal tissues absorbs. More Al^{3+} in contrast with others; therefor, in these patients, measuring the amount of Al^{3+} in the blood of the patient is indispensable.



Fig. 2. Some disadvantages of aluminum.



Fig. 3. Aluminum's exposure: A schematic which explores relationships between exposure, immediate targets mediating exposure, sinks and sources of biologically available aluminium with putative mechanisms of action and finally excretion of aluminium.

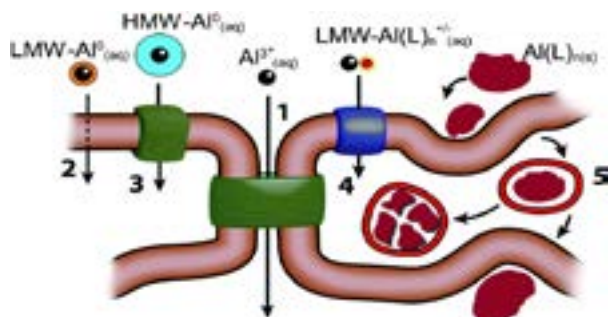


Fig.4. There are 5 major routes by which aluminium could be transported across cell membranes or cell epi-/endothelia; (1) paracellular; (2) transcellular; (3) active transport; (4) channels; (5) adsorptive or receptor-mediated endocytosis. There are 5 major classes of forms of aluminium which could participate in these transport routes. These are shown in the figure as; the free solvated trivalent cation ($\text{Al}^{3+}_{(\text{aq})}$); low molecular weight, neutral, soluble complexes ($\text{LMW-Al}^0_{(\text{aq})}$); high molecular weight, neutral, soluble complexes ($\text{HMW-Al}^0_{(\text{aq})}$).

The patients who have suffered chronic renal failure must be in intravenous therapy, and the rate of Al in their blood must be measured after each stage of removing dialysis fluid. Nowadays some researches about the relation of the amount of Al^{3+} and dementic mechanisms of intestinal absorption had better be carried out. Moreover there are a lot of analytical approaches for determining the amount

of Al^{3+} in water, human body, and biological samples. Among the methods which have been used for measuring the amount of aluminum in water industry, colorimetric and fluorimetric are common (widespread) methods which have been used. A kinetic fluorimetric approach with a claimed limit of detection of $0.13 \mu\text{g/L}$ using 1.0 ml of serum has been described by Iannou and piporaki. The results which have been obtained by fluorimetric method is similar to the results which have been obtained by electrothermal atomic absorption spectrometry (ETAAS). For an analysis that more than 1.0 mL of serum is used, the method of conventional fluorophore, lumogallion which has been presented by Suzuki et al is suggested. In the mentioned methods which have been being used for measuring the amount of Al^{3+} , the precipitation of protein, as well making agents occurs. Moreover, in the two mentioned approaches, pH must be controlled carefully. Moreover, in colorimetric and fluorimetric approaches, cationic interferences can be overcome by masking agents. In addition, the two methods may be applied for analyzing serum, but the pros or benefits of the approaches are less than electrothermal atomic absorption spectrometry (ETAAS). In the methods, reagents and equipment which have been required are cheap. The methods

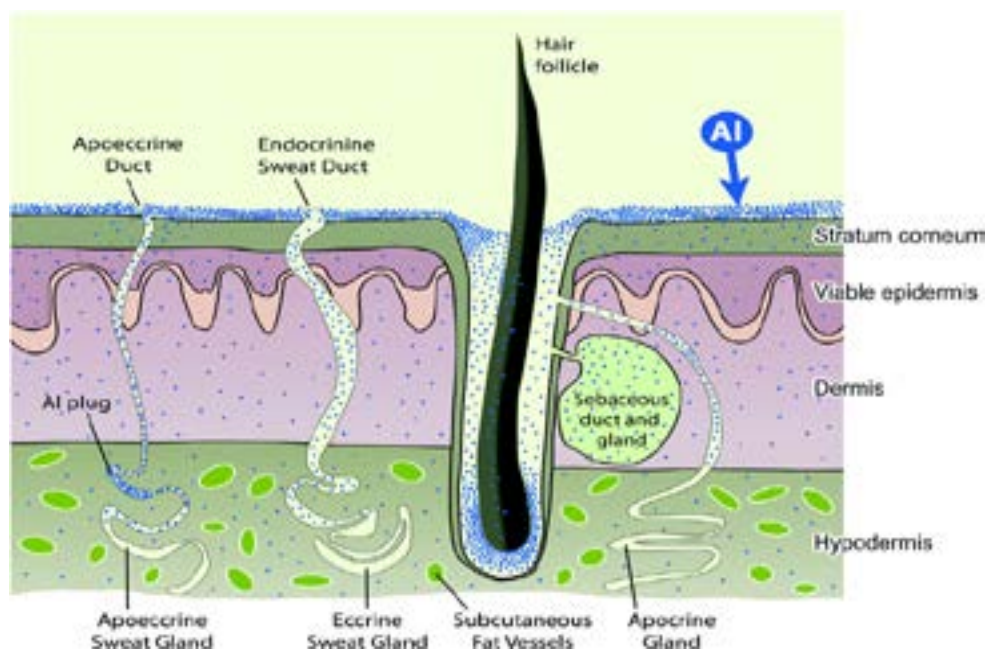


Fig. 5. The skin is a sink for topically applied aluminum and will act as a source of biologically reactive aluminum both to structures within the skin and to the systemic circulation.

of colorimetric and fluorimetric can be used for screening samples which have contamination in themselves. Also, the approaches are constructive for analyzing dialysis concentrates.

The procedure of chelation with eight-hydroxyquinoline when pH is equal to 6 and isobutyl methyl ketones is extracted into 10 ml has been suggested by Mazzeo and Lourenzyi for determining Al^{3+} in 200 ml of dialysis fluid concentrator by FAAS. A detection limit of $30\mu\text{g/l}$ has been obtained. Moreover no interferences from the high salt content of the concentrates have been found. Also, after analyzing the samples which have been dissolved in acid and ashed at 800°C by FAAS, it has been found out that the migration of aluminum occurs at the pH which is equal to 2 while the storage is prolonged and temperature is increasing. Marcin Frankowski et al have used some approaches such as GF-AAS, ICP-AES, and ICP-MS to determine the amount of Al^{3+} in groundwater samples. Moreover, inorganic aluminum complexes have been modeled by them. Their studies have been focused on some ground water samples which have been selected from the Miocene aquifer of the city of Poznan, located in Poland. The amount of Al^{3+} in the aquifer is variable – from 0.0001 to $725\mu\text{g/L}^{-1}$. Three analytical methods, i.e. graphite furnace atomic absorption spectrometry (GF-AAS), inductively coupled plasma atomic emission spectrometry (ICP-MS), and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for measuring the amount of aluminum in the groundwater have been used. The results which have been obtained from analytical methods have been used to determine the trend of groundwater from the Mesozoic aquifer to the Miocene aquifer. Distribution of Al^{3+} has been modeled by Frankowski et al in 2011. After modeling, the existence of aluminum hydroxyl complexes in some parts of the groundwater has been confirmed [68]. In addition, based on the study which has been carried out by Frankowski et al in 2011, in spite of the fact that sulphates and organic matter in the most of groundwater samples are dominant, the aluminum complexes

have never participated in the reaction with the ligands (based on the modelling) [68]. Also, the change of the amount of aluminum concentration in groundwater aquifers due to aluminum's amphoteric property causes that fauna and flora will be ruined. Moreover, the low concentration of aluminum in groundwater aquifer are obtained when the transformations of aluminosilicates occur in the active water exchange zone. Soluble complex bonds with dissolved fluoride (AlF_2^{2+} , F_2^{+} , AlF_3^0 , AlF_4^{-}), Sulphate (AlSO_4^{+} , $\text{Al}(\text{SO}_4)^{2-}$), phosphate (AlHPO_4^{2+} , AlHPO_4^{+}) ligands.

With low – molecular organic acids are the major sources of aluminum in groundwater. In most aquifers, based on their studies, Al^{3+} and hydroxide complexes as exchangeable aluminum fractions are the main sources of aluminum [68]. Moreover, the penetration of Al^{3+} , AlOH^{2+} , and $\text{Al}(\text{OH})_2^{+}$ into the agricultural products causes toxicity to humans. Based on the research which has been carried out by Frankowski et al in 2011, the high concentrations of aluminum in groundwater aquifers demonstrate that hydroxide complexes and organic complexes are dominant in the aquifers [68]. The concentration of trace aluminum in groundwater, surface water, the river have been usually determined by using GF-AAS (graphite furnace Atomic Absorption spectrometry). In addition, for measuring the amount of aluminum in limed lakes, forest soil waters, and springs, using inductively coupled plasma mass spectrometry (ICP-MS) is suggested. Also, for determining the amount of aluminum in drinking water, inductively coupled plasma Optical Emission spectrometry (ISP – OES) has been used. Based on some researches, inductively coupled plasma mass spectrometry method is not constructive for determining the amount of aluminum in water due to the interferences which have been caused by other elements in water samples.

4. Conclusions

In this research paper, the importance of measuring the amount of aluminum complexes in the nature (soil and water) and human bodies has been paid

attention to. Also, some researchers which have been carried out have been selected and assessed. All researches have tried to present the best analytical methods which are more accurate and precise for determining the amount of aluminum in water, soil, and biological samples. From 1985 to 2018, the limit of detection has become lower, and limit of quantification has extended. Nowadays, the approaches which have been used are more precise, time-consuming, cost-effective, and applicable. Also. At the present time, nano-absorbents are used for separation of Al^{3+} from blood of human tissues, water, soil, and plants' tissues. Between 2016 and 2017, flame atomic absorption spectrometry has been used to determine the amount of aluminum in tricalcium phosphate anhydrous powder which contains about 350mg/Kg^{-1} aluminum in itself. From 2011 up to now, for determining the amount of Al^{3+} in some top and well water samples, in some areas of Iran, surfactant cetyltrimethylammonium bromide and. The method of cloud point extraction have been used with each other. From 2013 to 2019, for quantifying the amount of Al^{3+} in waters and soft drinks of the country of Thailand, spectrophotometric approach using eriochrom cyanine has been used. Also, in this method, the limit of detection is less than 0.0008 and the limit of detection is about 0.0125 mg/L^{-1} . From, 1982 up to now, for quantifying the amount of aluminum in human blood, serum, urine, and tissues, in some European hospital, using electro-thermal atomic absorption spectrometry has been suggested. In the decade of 1990, in the hospital of USA, for determining the amount of aluminum in blood, the method of diluting plasma samples with HNO_3 /Triton X-100, matrix modifier fourfold was used. Moreover, for measuring the amount of aluminum in the patients who have suffered less renal failure, or their renal functions are normal, diluting samples with an equal volume of $Mg(NO_3)_2$ matrix modifier and atomizing the samples from a L'vov platform were usual methods. Also, based on the studies which have been carried out from 2009 to 2019 about the determination of aluminum in groundwater aquifers, in most parts

of Eurasia and USA, the concentration of trace aluminum in groundwater, surface water, and river have been usually quantified by using GF-ASS (graphite furnace atomic absorption spectrometry); moreover, for measuring the amount of aluminum in limed lakes, forest soil waters, and springs, using inductively coupled plasma mass spectrometry (ICP-MS) has rarely been suggested. In addition, for determining the amount of aluminum in drinking water, inductively coupled plasma optical emission spectrometry (ICP-OES) has been used. Also, since 2017 to 2019, in some groundwater aquifers of London, chemometric methods using optimization algorithms have been common among a lot of researchers, scientist, and hydrogeologists for determining the amount of aluminum. Furthermore, based on most researches, when pH is more than 7.0, the solubility of aluminum increases, and then water is polluted. Afterward, lot of people will suffer renal failure or chronic renal failure.

5. Nomenclatures

CNS: Central Nervous System

CPE: Cloud Point Extraction

ETAAS: Electrothermal Atomic Absorption Spectrometry

GONPs: Graphene Oxide Nanoparticles

GF-ASS: Graphite Furnace Atomic Absorption Spectrometry

IL: Ionic liquid

ICP-MS: Inductively Coupled Plasma-Mass Spectrometry

ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry

LR: linear range

LOD: limit of detection

PF: Preconcentration Factor

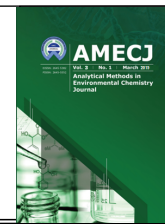
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Biochemistry Method: Simultaneous determination of formaldehyde and methyl tert-buthyl ether in water samples using static headspace gas chromatography mass spectrometry

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ABSTRACT

The present study describes a method based on static headspace extraction (HS) followed by gas chromatography/mass spectrometry (GC/MS) for the qualitative and quantitative analysis of methyl tert-buthyl ether (MTBE) and formaldehyde (HCHO) in water samples. Cytochrome P450A6 has important role for converting of MTBE to tert-butyl alcohol (TBA) and HCHO. To enhance the extraction capability of the HS, extraction parameters such as extraction temperature, extraction time, the ratio of headspace volume to sample volume and sodium chloride concentration have been optimized. Wide linearity range was verified in a range of 5-10000 $\mu\text{g L}^{-1}$ for MTBE ($r^2=0.9998$), while those for HCHO was 5-500 $\mu\text{g L}^{-1}$ ($r^2=0.9996$). Detection limits for MTBE and HCHO was 1.0 $\mu\text{g L}^{-1}$ and 1.3 $\mu\text{g L}^{-1}$, respectively. Best results were obtained when the analyzed oily water samples were heated to 70 °C for 20 min, with the sample volume 10 mL in 20 mL vial, and NaCl 30% (w/v) was used to saturate the samples. The proposed analytical method was successfully used for the quantification of analytes in water and wastewater samples.

Keywords:

Formaldehyde

MTBE

Static headspace-GC/MS

Oil refining

Wastewaters and Water

1. Introduction

Formaldehyde (HCHO) is the most widespread carbonyl compound in the atmosphere. It enters the environment from natural sources (including forest fires) and from direct human sources such as fuel combustion, industrial on-site uses, off gassing from building materials and consumer products. Although formaldehyde is a gas at room temperature, it is readily soluble in water. Formaldehyde is very active, and is transported in air, water and contaminated soils. In aqueous

systems, atmospheric deposition is a significant source of formaldehyde [1], and in drinking water formaldehyde arises mainly from the oxidation of natural organic matter during ozonation [2] and degradation of oxygenates such as methyl tert-buthyl ether (MTBE) and dimethyl carbonate (DMC) [3]. It also enters drinking water via leaching from polyacetal plastic fittings in which the protective coating has been broken [4]. Formaldehyde is a very toxic compound and has been classified as a human carcinogen by the international agency for research on cancer (IARC), and also as a probable human carcinogen by the US. Environmental Protection Agency [5]. The

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national institute for occupational safety and health (NIOSH) considered formaldehyde as immediately dangerous to life and health at 24 mgm^{-3} ($20 \text{ } \mu\text{gmL}^{-1}$) [6]. It can damage the person's nerve system, lung and liver, and cause irritation of eyes, nose, throat and skin. Therefore, formaldehyde is one of the analytical interesting substances as a marker of fuel additive degradation. Its determination becomes also a hot spot of the research especially in oily wastewater matrices. A variety of methods for the determination of formaldehyde have been reported, including spectrophotometry [7-13], flow-injection catalytic method [14], high performance liquid chromatography [15], gas chromatography [16, 17], isotope dilution mass spectrometry [18], fluorimetry [19, 20], chemiluminescence [21,22], polarography [23], Fourier Transform Infrared Absorption [24] and sensors [25-28]. MTBE is also a volatile organic compound (VOC) produced from natural gas. It is primarily used for the oxygenation of fuel to enhance octane number and to improve the combustion process, in order to reduce carbon monoxide emissions [29]. MTBE readily dissolves in water, and moves rapidly through soils and aquifers. It is resistant to microbial decomposition and difficult to remove in water treatment. Its occurrence in the environment is of a great concern because of the toxicity of MTBE and its degradation products [30]. Since MTBE is highly volatile and very soluble in water, it can be easily found both as airborne pollutants of living and working environments and as contaminants of drinking water [31]. To date limited data are available on the effects of MTBE on health. Notwithstanding this, USEPA has concluded that at high doses, MTBE is a potential human carcinogen and recommended that MTBE levels in drinking water be kept below a range of 20-40 ppb [32].

MTBE and other oxygenates in ground waters are frequently measured using standard US EPA approved methods (e.g., EPA 8021B, EPA 8260B, ASTM D 4815). These procedures usually perform gas chromatographic separation coupled with photo ionization detector (PID), flame ionization detector (FID) or mass detector (MS). The introduction of analytes in the chromatographic apparatus is performed either via direct injection of water samples (DAI) [33,34], or using sampling techniques as dynamic headspace (P&T), static headspace [35], solid phase microextraction (SPME) [36-44], and solvent microextraction (SME) [45,46]. The DAI technique presents some difficulties to be coupled with capillary GC, due to the large expansion volume of water. Direct water injections are prone to back flush in the injector port, which can cause loss of analyte response as well as injection port contamination. MTBE oxidation can generate tert-butyl alcohol (TBA) and formaldehyde (Fig.1). Our previous study demonstrated that human cytochrome P450 2A6 is able to metabolize MTBE to tert-butyl alcohol (TBA) and formaldehyde, a major circulating metabolite and markers for exposure to MTBE [3]. CYP2A6 plays a significant role in metabolism of gasoline ethers in liver tissue. The purpose of this present study is to develop a simple, sensitive and selective method for simultaneous determination of trace amounts of formaldehyde and MTBE in environmental and water samples. To our knowledge, no method was found in the literature for this case.

2. Experimental

2.1. Chemicals and Standard Solutions

In this work, analytical grade of chemicals and reagents were purchased from Merck, Germany.

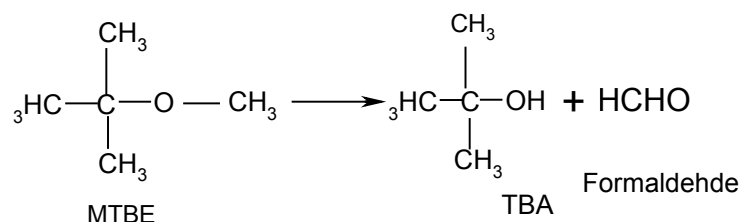


Fig. 1. MTBE oxidation reaction

Double distilled water (DDW) was used for preparation and dilution of samples. Helium and nitrogen (ultrapure carrier grade) were obtained from Roham gas Company (Tehran, Iran). An aqueous formaldehyde stock solution, 1000 gm L⁻¹, was prepared by diluting 2.5mL of 37% w/v stock formaldehyde solution (Merck) to 1 L with deionized distilled water (DDW) and was standardized by the sulfite method [47]. Working solutions of formaldehyde were subsequently prepared by appropriate dilution of the stock solution with DDW. MTBE Calibration stock solutions were prepared by adding 10 µL of pure MTBE (99.5%, Merck) to 10 ml of MeOH (Merck) in a 10ml vial with a PTFE-silicon septum. The mixture was manually agitated for 5 min. The first dilution steps were performed with methanol whereas further preparation of the standard solutions was carried out with DDW. The standard solutions used within 4 weeks. All sample and standard vials were completely filled to eliminate headspace. Individual and cumulative working standard solutions were obtained by appropriate dilution of the stock in 50 ml of methanol and further diluted in ultrapure Milli-Q water to prepare solutions containing MTBE and formaldehyde at the nanogram per milliliter level. The method was optimized with MTBE and formaldehyde solutions of 50 µg/L⁻¹ concentration. It should be noted that in this work Methyl ethyl ketone (MEK) (50 ng mL⁻¹) was used as internal standard in environmental and biological samples.

2.2. Apparatus and Procedure

Static headspace analysis was performed using a CTC-CombiPAL autosampler (Bender and Holbein, Zurich, Switzerland) mounted on top of a GC-MS system. The autosampler was equipped

with a heatable CTC agitator for incubation and shaking, and a robotic arm. To prevent the carry over of analytes, we used a heated flushing station for conditioning of the HS needle and reconditioning after each analysis. Both the gas station and the heated flushing station were flushed with nitrogen. The syringe body was held in the syringe adapter heater. 20 mL vials sealed with screw top caps with PTFE/silicon septa were used. Parameters of the instrument are shown in Table 1. A salt content of 30 (% w/v) was chosen for the quantitative determination of target analytes in environmental and human biological samples.

The GC-MS analysis was performed using a Varian (CP-3800 series) gas chromatograph equipped with a mass-selective detector (Varian, quadrupole 1200) and a factor-four, VF-5ms fused-silica capillary column with a 30m × 0.25 mm i.d. and 250 µm film thickness (Varian) was used. The GC conditions were as follows: inlet temperature, 250 °C; inlet mode, split operation with split ratio 1:25. The oven temperature was set at 50 °C and raised to 100 °C at 5°C/per min, and raised to 275 °C at 20 °C per minute. The final temperature was maintained for 1.75 min and the total run time was 20 min. Helium, at a constant flow rate of 1.5 ml/min was used as the carrier gas. Mass spectra were obtained at 70eV in the electron impact ionization mode; the spectrometer was operated in the full scan mode over the mass range from 75 to 110(m/z). The source, transfer line and quadrupole temperatures were maintained at 200°C, 250 °C and 200 °C, respectively. Total ion current chromatograms were acquired and processed using Workstation data analysis software (Varian). To increase sensitivity, the selected ion monitoring (SIM) mode was applied in quantitative analysis. The most abundant ion was used as the quantified ion. In Table 2, some

Table 1. Headspace conditions

Syringe Temperature : 71°C	Plunger fill speed: 100 µLper sec
Agitator Temperature : 70°C	Pre-injection delay: 4 sec
Sample incubation time: 20 min	Plunger injection speed:250 µLper sec
Agitator speed: 500 rpm	Syringe flush time:120 sec
Agitation cycle: 2 sec on, 4 sec off	sample volume, 10 ml in 22 ml vial

Table 2. Analytical conditions of MTBE, formaldehyde and methyl ethyl ketone by GC-MS with SIM

Compound	Molecular weight	Retention time (min)	Quantification ions (m/z)
Formaldehyde	30	1.39	30
MTBE	88	1.45	73
Methyl ethyl keton	73	1.90	43

analytical conditions of MTBE, formaldehyde and methyl ethyl ketone by GC-MS with SIM mode are shown. All quantifications made in this study were based on the relative peak area of analytes to the internal standard from the average of three replicate measurements in environmental and biological samples.

3. Results and discussion

Various parameters were evaluated during the method development. In the present study, the evaluation of individual parameters was carried out while all other method parameters were kept constant.

3.1. Extraction temperature

The temperature of sample affects on evaporation of analyte into the headspace. We expected that an increase in sample temperature will result in improved the extraction efficiency, because of the increased evaporation of the analyte concentration in the headspace. The effect of sample temperature was studied by changing the sample temperature from 40 to 80 °C. As can be seen in figure 2, the

amount of extracted analyte (into the headspace) increases with increasing temperature up to 80 °C. In headspace analysis, it is recommended not to use high temperatures (in order to avoid the over-pressurization of the vial sample, and so avoid accidents) and, therefore, an extraction temperature of 70°C was selected in environmental and biological samples. The syringe temperature of 5°C above vial temperature was selected to avoid the analytes condensation.

3.2. Extraction time

The time required for the extraction process was an important parameter to be investigated. The most adequate time for the HS extraction was considered to be the time reaching the equilibrium of the analytes between the vapor phase and aqueous phase. Extraction time between 5 and 30 min were tested for the samples of 50 µg L⁻¹ at 70°C, and the heating-time profile for the MTBE and formaldehyde mixture is shown in figure 3. An increasing efficiency was observed for both

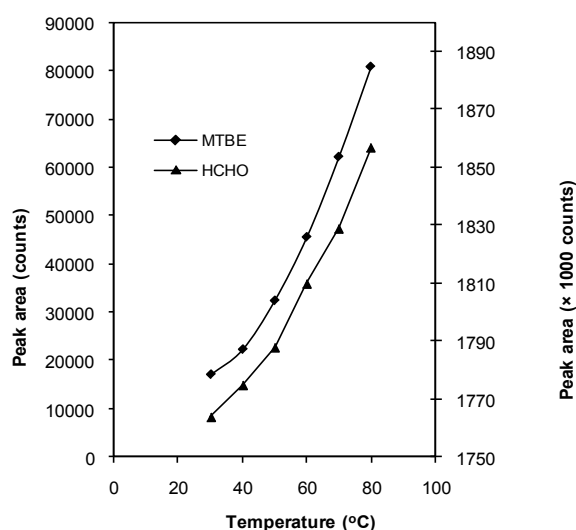


Fig. 2. Influence of the extraction temperature on the relative peak areas of 50 µg L⁻¹ MTBE and formaldehyde in water.

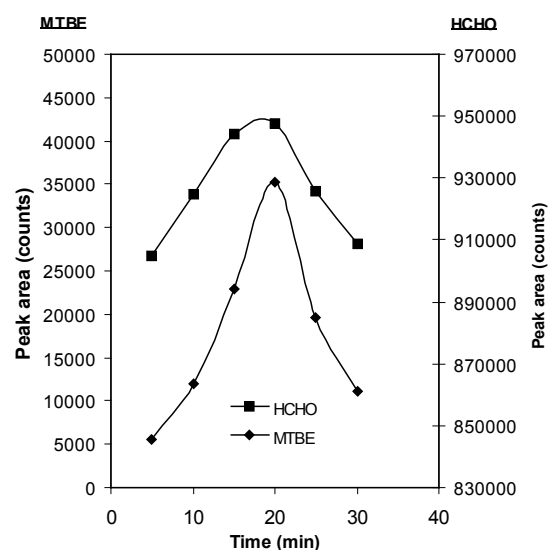


Fig. 3. Effect of extraction time on peak areas of 50 µg L⁻¹ MTBE and formaldehyde in water at 70 °C.

compounds when the longer extraction time was used until 20 min, and then an increase in extraction time caused a decrease in the efficiency. A reason for this phenomenon was the transfer of water molecules to headspace which diluted the gas phase and decreased extraction amounts. So the extraction time of 20 min was considered for the subsequent experiments.

3.3. Ionic strength influence

Because the ionic strength of the solution influences the partition coefficient between the gas and liquid phase (K) the effect of salt amount on extraction efficiency was also checked. The effect of the salt on the extraction efficiency was investigated by comparing the extraction efficiency of samples which contained different amounts of sodium chloride (NaCl) from 0 to 40 (%w/v), and its influence, as the salting out agent, on the ion abundance of GC-MS chromatogram for MTBE and formaldehyde is shown in figure 4. As can be seen the addition of salt does not have the same effect for both target analytes: the addition of NaCl led to better results in the case of MTBE, while for the HCHO no favorable, and sometimes unfavorable effects (when more than 30% (w/v) of sodium chloride were employed) were observed. In human blood, the effect of different ions on extraction of Formaldehyde and MTBE based on proposed procedure was investigated. The interference of some coexisting ions in water and wastewater samples on the recovery of Formaldehyde and MTBE was studied under optimized condition. The proposed procedure was performed using a 10 mL sample containing 5-500 $\mu\text{g L}^{-1}$ of formaldehyde and MTBE and 2 mg L^{-1} of different concentration of matrix ions such as, Zn^{2+} , Cu^{2+} , Mn^{2+} , Na^+ , K^+ , Ca^{2+} and Mg^{2+} . The tolerate amounts of important ions and biological matrix (albumin and proteins) were tested that caused less than 6% of the head space extraction alteration. In optimized conditions, the ions and biological matrix do not interfere to formaldehyde and MTBE extraction by procedure (less than 5%). The results showed us, the most of the probable waste matrix concomitant have no

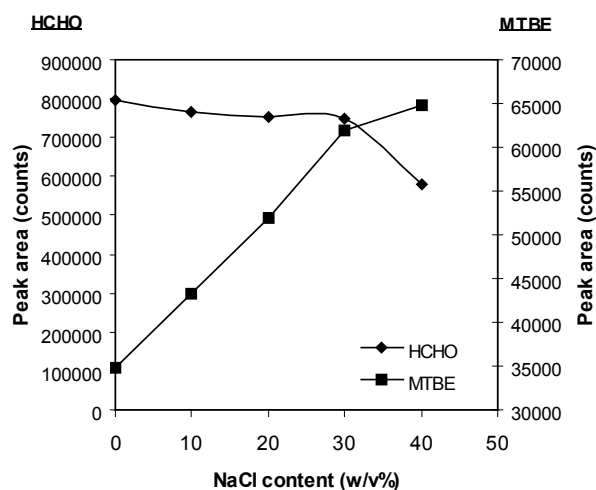


Fig. 4. Effect of NaCl additives on detector response areas of 50 $\mu\text{g L}^{-1}$ MTBE and formaldehyde in water produced by HS for 20 min at 705 °C and sample volume 10 mL in 20 mL vial

considerable effect on the recovery efficiencies of formaldehyde and MTBE.

For MTBE the headspace extraction efficiency is increased with increasing concentration of salt in environmental samples and it reached the peak yield when NaCl (30%, w/v) was used to saturate the samples. The reason was considered to be the increase of ionic strength in aqueous samples by adding salt, therefore the solubility of analytes was decreased and more analyte was released into the headspace. For HCHO the observed behavior could be explained on account of its high solubility in water (37%) and strong interaction by solvent molecules (water) through hydrogen bonding that cause a greater affinity for water samples. Therefore, 30 % (w/v) salt content was chosen for the quantitative simultaneous determination of both target analytes.

3.4. Sample volume

The ratio of sample volume to headspace volume is an important parameter that affects the extraction efficiency of HS. An increase in sample volume and, consequently, a decrease in headspace volume enhance the extracted amount of analyte, which improves the sensitivity. The optimal ratio of the aqueous volume to the headspace volume for headspace analysis in 20 mL vials was determined by varying the sample

volume from 5 mL (1/4 vial volume) to 15 mL (3/4 vial volume). The results are also shown in Figure 5. The extracted amounts of analytes increase continuously with increasing sample volume reach a maximum at an aqueous volume of 10 ml and then decrease because of the decreased volume of the headspace. In the work, sample volume of 10.0 mL (in 20.0 mL vial) was used.

3.5. Evaluation of the method performance

Figure 6 shows a typical total ion chromatogram (TIC) of a standard solution containing, 100 $\mu\text{g L}^{-1}$ of TBE and HCHO after its headspace extraction under optimal experimental conditions in wastewater and environmental samples. The linearity, limits of detection and precision were calculated when the optimum conditions for the HS-GC-MS procedure were established. The linearity of the method was examined by spiking DDW with MTBE and HCHO in a concentration range from 5 to 10000 $\mu\text{g L}^{-1}$ in water samples and 5 to 500 $\mu\text{g L}^{-1}$ in biological samples. Each solution was submitted to the HS-GC-MS analysis three times. The figures of merit of the calibration graphs are summarized in Table 3. A plot of the peak areas against the concentrations of standards was obtained (Fig.7). Lack-of fit test was performed to check the goodness of fit and linearity

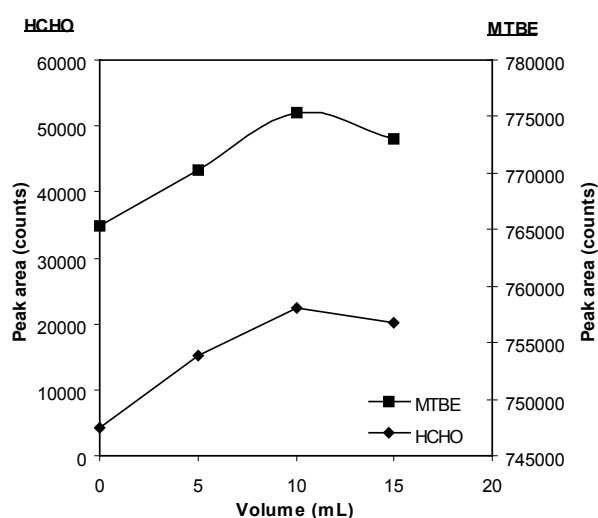


Fig. 5. Effect of solution volume in 20 ml vial on peak areas of 50 $\mu\text{g L}^{-1}$ MTBE and formaldehyde in water produced by HS for 20 min at 70 °C.

[48]. Lack-of-fit test demonstrated that the linear models were adequate because the whole p values were more than 0.05 at significance level of 95%. (Table 4). The linear range experiments provided the necessary information to estimate LODs, based on the signal that differed three times from the blank average signal, was 2 and 5 $\mu\text{g L}^{-1}$ for MTBE and HCHO, respectively. Analytical accuracy was assessed from the recovery of analyte spiked to various of biological and environmental samples (Table 5). The repeatability expressed as the relative standard deviation (R.S.D.) was obtained by carrying out five replicate assays on each water samples (Table 2), and gave a value less than 4.8% and 2.6% in biological and environmental samples, respectively. Therefore, this method is deemed acceptable for determining of trace level of $\mu\text{g L}^{-1}$ in water and biological matrix.

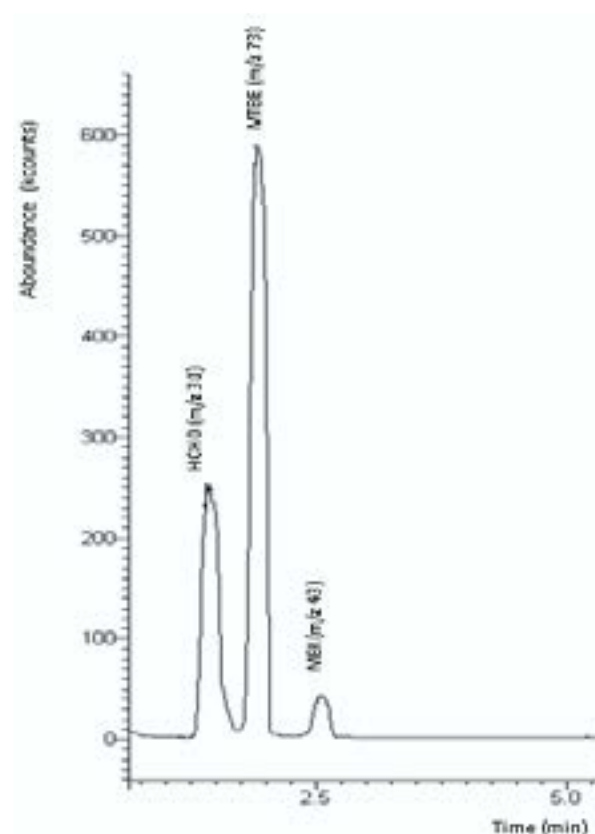


Fig. 6. Total ion chromatogram (TIC) in SIM mode of an ultrapure water solution contaminated with MTBE (50 $\mu\text{g L}^{-1}$) and formaldehyde (50 $\mu\text{g L}^{-1}$), extracted using static headspace. Extraction conditions: Extraction time: 20 min, Extraction temperature: 70 °C, sample volume 10 mL in 20 mL vial and NaCl 30% (w/v).

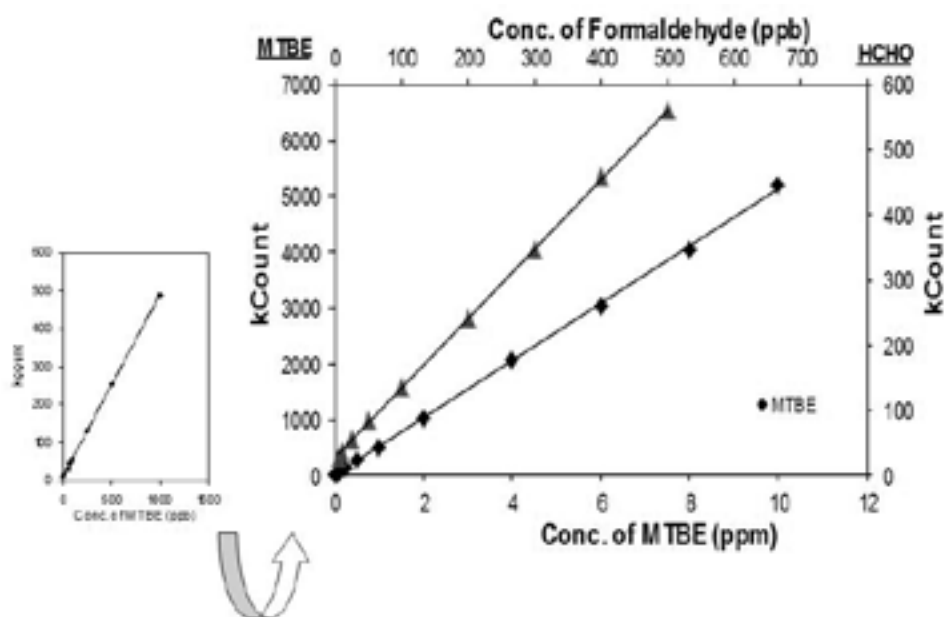


Fig. 7. Standard calibration curves of peak areas against the concentrations of MTBE (◆) and HCHO (■). MTBE: $y = 14.90x + 28.32$ ($r = 0.996$), HCHO: $y = 61.07x + 88.88$ ($r = 0.998$).

Table 3. Analytical figures of merit of the determination of MTBE and HCHO ($\mu\text{g L}^{-1}$)

Compound	Regression Equation ^a	Linear Range	LOD	RSD (%, n = 5)	
				0.1	40
MTBE	$y = 513.24x + 0.319$	5-10000	2	4.8	6.8
formaldehyde	$y = 1.759x + 27.53$	5-500	5	1.9	7.8

^a y: Analyte area-to-internal standard area, x: concentration ($\mu\text{g L}^{-1}$).

3.6. Analysis

The proposed method was firstly used to quantify MTBE and HCHO in wastewaters related with Tehran oil refinery and human blood and urine of petrochemical workers. The obtained results in Table 5, were showed good recoveries, and the method was ideally suited for these matrices. The synthetic biological samples were also analyzed by the develop method (Table 6). Here, blank is containing 500 μl mixture of 50 mM tris-HCl buffer (pH=7.4), 1mM NADPH (as inducer), 10 mM MgCl_2 and 150 mM KCl (as electrolytes). Synthetic sample 1 is prepared by addition of 5.02 $\mu\text{g ml}^{-1}$ MTBE in the blank solution.

Samples 2 and 3 are also the same synthetic sample 1 that are treated by 20 picomol of human cytochrome P450 (2A6), prepared from Sigma-Aldrich Co., at 37 °C for 13 and 30 minutes, respectively. Cytochrome P450 (2A6) is known as one of the most effective enzymes in metabolism alkoxyethers. In order to control enzyme activity and termination of reaction time, it was need to a deactivator such as 100 μl of 0.10 M perchloric acid. Formaldehyde was also a mainly byproduct of enzymatic degradation reaction of MTBE and was detected by developed method as given in Table 6. In the case of formaldehyde, although the calculated values can be estimated stoichiometrically.

Table 4. Evaluation of the goodness of fit and linearity of calibration graphs

Compound	Correlation coefficient, r	Determination coefficient, R^2	Lack-of-fit, p^a
MTBE	0.9998	0.9993	0.089 > 0.05
Formaldehyde	0.9996	0.9984	0.078 > 0.05

^a Confidence interval, 95%.

Table 5. Determination of HCHO and MTBE in water and Human samples at optimum extraction conditions ($\mu\text{g L}^{-1}$)

Water	Tap water				Well water ^c			
	Conc.	^a Added	Found	Recovery (%)	Conc.	^a Added	Found	Recovery (%)
HCHO	ND ^b	25.0	25.2 $\pm$ 2.8	100.8	ND ^b	25.0	23.9 $\pm$ 4.2	95.6
MTBE	ND ^b	25.0	24.4 $\pm$ 4.8	97.6	12.0	25.0	36.2 $\pm$ 3.1	97.0
Wastewater	Oil company				Petrochemical			
	Conc.	^a Added	Found	Recovery (%)	Conc.	^a Added	Found	Recovery (%)
HCHO	22.1	20.0	41.4 $\pm$ 2.3	96.5	12.8	10.0	22.5 $\pm$ 4.2	97.0
MTBE	16.3	20.0	36.9 $\pm$ 1.5	103.1	9.7	10.0	19.3 $\pm$ 3.1	96.0

^a Mean of triplicates with percent R.S.D (n=5).^b Not found.^c Well water nearby Tehran oil refinery.

standard method based on derivatization with 2, 4-dinitrophenylhydrazine and HPLC detection was used to assay the values[49]. An average recovery of 65.5 and 91.7 % was obtained for degradation process of MTBE after passing 13 and 30 min. from course of the reaction, respectively. The standard deviation of measurements at ppm levels was not greater than 2.6%.

4. Conclusions

An automated and simple method has been developed for simultaneous determination of MTBE and formaldehyde in water and human matrices. It was based on the use of HS device coupled with a GC–MS instrument. The no necessity of consumables or reagents for sample treatment made HS-GC–MS to be considered as the best extraction option of the studied ones. The analysis required 20 min of sample incubation or extraction time and less than 5 min for chromatographic determination programming the MS detector in SIM acquisition mode. Good precision and the simple sample preparation enable to use this procedure for routine investigations. This proposed method was applied to the analysis in water samples.

5. References

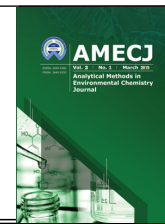
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Table 6. Simultaneous determination of MTBE and Formaldehyde in synthetic biological samples

No.	Sample	MTBE / $\mu\text{g ml}^{-1}$		Formaldehyde / μgml^{-1}	
		Calcd.	Found	Calcd.	Found
1	Synthetic sample 1	5.02	4.91	-	-
2	Synthetic sample 2	-	1.73	1.09	1.14
3	Synthetic sample 3	-	0.415	1.48	1.53

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Spectrofluorometric determination of L-tryptophan after preconcentration using multi-walled carbon nanotubes

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ABSTRACT

A solid-phase extraction method based on multi-walled carbon nanotubes (MWCNTs) was applied for the preconcentration of L-tryptophan (α -amino acid) prior to its spectrofluorometric determination. Due to the high surface area of MWCNTs, satisfactory concentration factor and extraction recovery can be achieved with only 10 mg MWCNTs in 5 min. The effects of pH, sorbent amount, eluent type and time on the recovery of the analyte were investigated. Under the optimum conditions, the detection limit for L-tryptophan was 8.9 ng mL⁻¹. The precision of the method, evaluated as the relative standard deviation obtained by analyzing of 10 replicates, was 2.6%. The practical applicability of the developed method was examined using wheat and barley samples.

Keywords:

L-tryptophan

Solid-phase extraction

Multi-walled carbon nanotubes

Bioanalysis

Spectrofluorometry

1. Introduction

Analysis of amino acids is important in several fields of research, particularly in food, soil, biotechnology and pharmaceutical industries [1, 2]. Tryptophan (2-Amino-3-(1H-indol-3-yl) propanoic acid) (Trp) is an essential amino acid for humans and is required for the biosynthesis of proteins and also is important in nitrogen balance in adults. This amino acid cannot be synthesized in the human body and must be obtained from food or supplements. Tryptophan is sometimes added

to food products and pharmaceutical formulas to correct possible dietary deficiencies [3]. Therefore, reliable analytical methods for the determination of Trp are of great interest.

A variety of analytical methods have been described for the determination of Trp, including high performance liquid chromatography (HPLC) [4], capillary electrophoresis [5], electroanalytical methods [6], spectrophotometry and spectrofluorimetry [7, 8]. Compares with the Chromatographic methods, spectrofluorimetric determination is a simple, fast and inexpensive method. However, the direct determination of Trp at low concentrations by spectrofluorimetry

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is difficult because of insufficient sensitivity of this technique as well as the matrix interferences occurring in real samples, and an initial sample pretreatment, such as preconcentration of the analyte, is often necessary [9, 10].

Solid phase extraction (SPE) is a routine extraction method for preconcentration of organic and inorganic analytes. This technique reduces solvent usage and exposure, disposal costs, and extraction time. Various adsorbents, such as octadecyl functional groups bonded on silica gel, C18 [11], silica gel [12], chelating adsorbents [13], Amberlite XAD resins [14, 15], activated carbon [16] and other sorbents [17] have been used for adsorption of analytes in SPE methods.

Multi-walled carbon nanotubes (MWCNTs) have received great attention due to their exceptional electronic, mechanical, thermal, chemical properties and significant potential applications in many fields [18]. Owing to their large surface area and high reactivity, MWCNTs based adsorbents have been used for solid phase extraction and preconcentration of organic compounds and metal ions [19, 20]. Compared with traditional SPE sorbents, MWCNTs offer a significantly higher surface area-to-volume ratio and a short diffusion route, resulting in high extraction capacity, low extraction time and high extraction efficiencies [21].

In this paper, a magnetic solid phase extraction method based on multi-walled carbon nanotubes is developed for the extraction and preconcentration of L-tryptophan(α -amino acid), prior to its spectrofluorometric determination.

2. Experimental

2.1. Reagents

All reagents used were of analytical grade and were used as supplied. NaOH, ammonia solution, were purchased from Merck (Germany). MWCNTs (purity > 95%) were obtained from Sigma-Aldrich. Standard stock solution ($1000 \mu\text{g mL}^{-1}$) of L-tryptophan was prepared by dissolving the pure solid (Sigma-Aldrich) in deionized water. Working solutions were prepared daily by adequate dilution

with deionized water.

2.2. Instrumentation

The fluorescence measurements were performed using a Perkin-Elmer LS50 spectrofluorometer, equipped with a xenon discharge lamp. A Metrohm model 744 digital pH meter, equipped with a combined glass-calomel electrode, was employed for the pH adjustments.

2.3. solid-phase extraction procedure

A 40 mL sample or standard solution containing L-Trp (pH 6) was transferred in a polypropylene centrifuge tube. Then 10 mg of MWCNTs was added into the sample solution. The mixture was shaken for 5 min. The solution was centrifuged for 5 min at 5,000 rpm, and the aqueous phase was removed. The preconcentrated target analyte was eluted using 1.0 mL of a 2 mol L^{-1} solution of NaOH. The pH of this solution was adjusted at 10 by addition of 2 mol L^{-1} hydrochloric acid and then solution made up to 2.0 ml with deionized water. Finally, the concentration of L-tryptophan was determined spectrofluorometrically at $\lambda_{\text{em}} = 360 \text{ nm}$ after excitation at 274 nm.

2.4. Sample preparation

For digestion of wheat and barley samples, 20.0 mL KOH (10 % m/v) were added to 0.20 g of sample powder in a 100.0 mL conical flask to hydrolyze in an oven at 40°C for 16–18 h. Then, the mixture was filtered through a filter paper and adjusted to pH 6 by the addition of 6 M HCl. Finally the solution made up to 50.0 ml with deionized water.

3. Results and discussion

3.1. Optimization of extraction conditions

3.1.1. Effect of pH

The effect of pH on the extraction of L-Trp was studied in the range of 3.0–11.0 using nitric acid or ammonium acetate. The resulting percent recovery-pH plot is shown in Fig. 1, which indicates that sorption is maximum and quantitative in the pH range 3.0–9.0. Therefore, pH 6.0 was selected for further study.

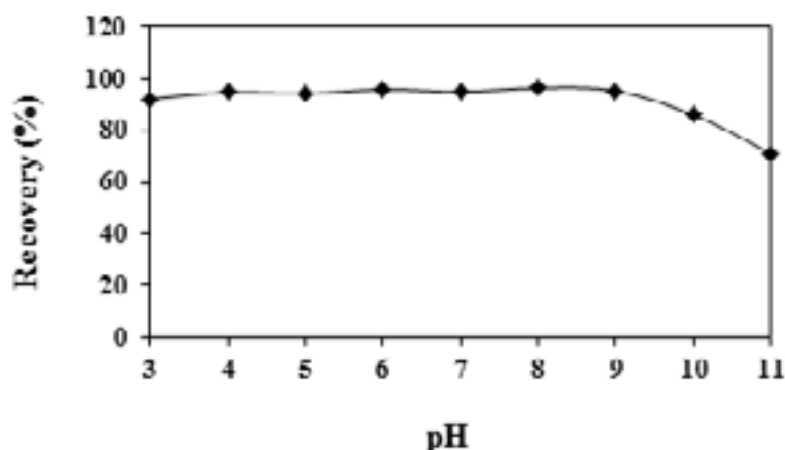


Fig. 1. Effect of pH on the extraction efficiency of L-Trp. Conditions: sample volume, 40 mL; MWCNTs amount, 10 mg; Concentration of L-Trp, $0.10 \mu\text{g mL}^{-1}$.

3.1.2. Effect of the sorbent amount

In comparison with the traditional sorbents, MWCNTs offer a significantly higher surface area-to-volume ratio. Therefore, satisfactory results can be achieved with fewer amounts of MWCNTs. In order to study the effect of the sorbent, 2 to 20 mg of MWCNTs was added to 40 mL of the sample solution (Fig. 2). The obtained results showed that by increasing the sorbent amounts from 2 up to 10 mg due to increasing accessible sites, extraction recovery increased and after that remained constant. A 10 mg of the MWCNTs was selected for subsequent experiments.

3.1.3. Effect of eluent type

In order to find the best eluent, different eluting solutions such as HCl, HNO_3 , acetic acid, NaOH, were tested. Obtained results showed that among the tested eluent, NaOH was found to be the superior solvent in comparison with other solvents for desorption of analytes from surface of the sorbent. Therefore, NaOH solution was selected and used as an eluent. The effect of NaOH concentration on the recovery of the adsorbed L-Trp was examined in the range of 0.1 to 5 mol L^{-1} (Fig. 3). Based on the obtained results, 2.0 mol L^{-1} NaOH was sufficient for complete elution of the adsorbed Trp on the sorbent surface. To achieve the highest recovery

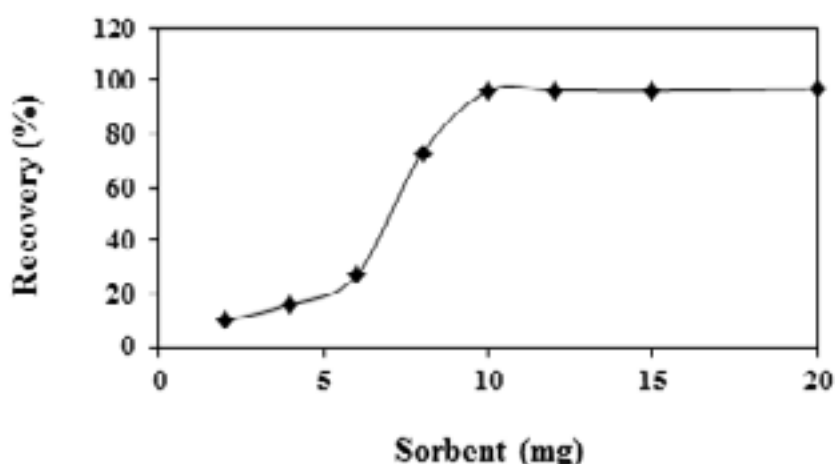


Fig. 2. Effect of the MWCNTs amount on the recovery of L-Trp. Conditions: pH, 6, sample volume, 40 mL; Concentration of L-Trp: $10 \mu\text{g mL}^{-1}$.

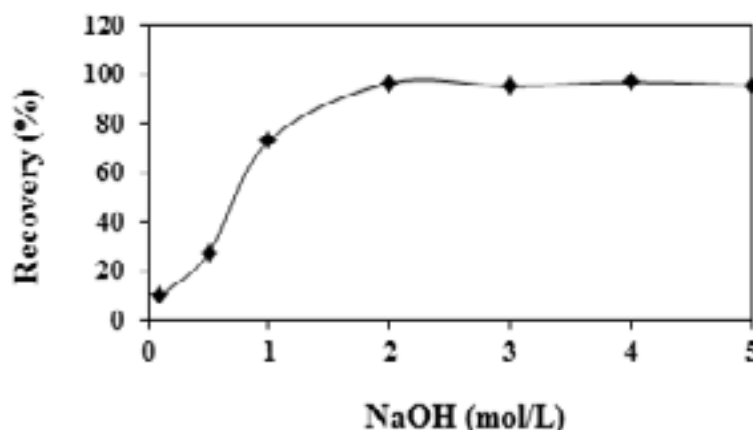


Fig. 3. Effect of NaOH concentration on the extraction efficiency of L-Trp. Conditions: pH, 6, sample volume, 40 mL; MWCNTs-Fe₃O₄ amount, 10 mg; Concentration of L-Trp, 0.10 $\mu\text{g mL}^{-1}$.

of the adsorbed L-Trp, the effect of the volume of the eluent was also tested. The minimum volume of NaOH required for quantitative elution of the retained analyte was 1.0 mL.

3.1.4. Effect of extraction time

The effect of extraction time on the extraction of L-Trp was studied in the range of 1–15 min. The experimental results indicated that there was no significant effect on the extraction efficiency when the extraction time increased from 5 to 15 min. Based on the above considerations, 5 min was selected for further studies.

3.1.5. Sorption capacity

In order to determine the maximum capacity for L-Trp, 20 mg of the adsorbent was added to 40 mL of an aqueous solution containing 20 mg L⁻¹ L-Trp and shaken it for 30 min under optimized conditions. After decantation of the sorbent, the concentration of retained L-Trp in the supernatant solution was determined. The maximum capacity was found to be 36.3 mg g⁻¹ for L-Trp.

3.2. Analytical figures of merit

Table 1 summarizes the analytical characteristics of the proposed method, including linear range, limit of detection, reproducibility, and enhancement factor. In the optimum conditions, a calibration graph was constructed by preconcentrating a series

of the solutions according to the procedure under experimental. The linear regression equation for the calibration graph for the concentration range of 0.04–3.40 $\mu\text{g mL}^{-1}$ was $I=92.69C+74.43$ ($r^2=0.9984$, $n=8$), where I is the fluorescence intensity and C is Trp concentration in the sample solution in $\mu\text{g mL}^{-1}$.

The limit of detection (LOD) of the proposed method for the determination of Trp was studied under the optimal experimental conditions. The LOD, defined as three times the standard deviation of 10 measurements of the blank solution divided by the slope of the calibration curve, was 8.9 ng mL⁻¹. The reproducibility of the proposed method for extraction and determination of 0.10 $\mu\text{g mL}^{-1}$ Trp ($n=10$) was also studied. The relative standard deviation (R.S.D.) of these determinations was 2.6 %.

3.3. Application

The proposed method was applied to the determination of L-Trp in wheat and barley samples

Table 1. Analytical parameters of the proposed method.

Parameter	Analytical feature
Linear range ($\mu\text{g mL}^{-1}$)	0.04–3.40
Calibration equation	$I=92.69C+74.43$
r^2	0.9984
LOD (ng mL ⁻¹)	8.9
R.S.D. % ($n=10$)	2.6

Table 2. Determination of tryptophan in food samples.

Sample	Tryptophan (mg/g)	
	Proposed method	HPLC
Wheat	1.54 ± 0.04	1.63
Barley	1.26 ± 0.03	1.14

and the obtained results by proposed method were compared with HPLC method. The results obtained are shown in Tables 2. The results demonstrated that the proposed method was suitable for the determination of L-Trp in real samples.

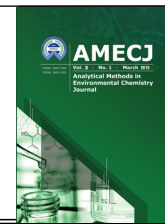
4. Conclusions

A simple and fast SPE method based on MWCNTs was developed for the preconcentration and spectrofluorimetric determination of L-Trp. The use of NPs ended the SPE method with high extraction capacity and preconcentration factors. Also using spectrofluorimetry as a detection system exhibits a low primary and operational cost in comparison with other methods such as HPLC. The method can be successfully applied to the separation and determination of tryptophan in real samples.

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Environmental Health Analysis: Assessing the emission levels of benzene from the fuel tanks doors of the vehicles in Tehran city

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ABSTRACT

In this study, 350 vehicles in 20 different models were examined in one of Tehran's Automobile Technical Inspection Centers. The laboratory tests indicate that longtime exposure to benzene has destructive effects on the blood cells, especially the bone-marrow cells. The concentration levels of benzene caused by the emission of gasoline vapors from fuel tanks doors were measured by PhoCheck EX5000 during a 5 to 15-minute interval for each car. The results indicate that the concentration of benzene caused by the emission of gasoline vapors from the fuel tanks door of the domestic cars was 10 times higher than the imported cars. In most of the imported cars, the amount of benzene in the three measured areas was negligible. This is due to the use of new technology and adaptation of strict environmental standards by the manufacturing country.

Keywords:

Volatile Organic Compounds

Benzene emission

PhoCheck

Domestic cars

Analysis of benzene in Air

1. Introduction

In recent decades, the various pollutants are being detected in urban areas which are mainly caused by fossil fuel components. They include a wide spectrum of hydrocarbons. The aromatic hydrocarbons are either bio-chemically or biologically active and are potentially carcinogenic or are by-products of benzene. Many of the recent

researches indicate the adverse effects of benzene on human health. Although VOCs are quite important, there have been few studies conducted in this regard in Tehran metropolitan [1-2]. The main emphasis has been on measurement, monitoring and control of VOCs in the last 10 years. The concentration of hydrocarbons in Tehran is much higher than other cities in the world (the benzene and butadiene 1 & 3 levels in Tehran are 10 and 18 times the permissible standards). [2].

Amongst the hydrocarbons, benzene due

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to its carcinogenic effects has an especial importance. The main sources of benzene emission in Tehran are the motor vehicles and the gas stations (due to the evaporation of fuel and lack of the fume control system). Majority of the vehicles in Tehran are run on gasoline and regrettably, their consumed gasoline has high benzene content (about 5% of the weight). Moreover, most of the automobiles manufactured domestically lack environmental standards. They can only attain Euro 2 Standard that was ratified in 1996. This is done through modifications in their appearance and the pollution control systems. Meanwhile, the production lines of reference companies like Peugeot 405 and Kia Pride have stopped abroad more than a decade ago. It is important to point out that the two major auto manufactures of Iran, namely SAIPA and Iran Khodro assemble the decade-old products of the aforesaid companies. [2]

Various studies are conducted on the effect of domestically produced fuel and vehicles' quality on air pollution. Similar researches are conducted in Brazil and Pakistan.[3-4]. Batterman in 2005 studied the amount of benzene emitted from the fuel tank. Based on his measurements, the average level of benzene emission was 2 milligrams per hour. For old vehicles, this amount reached 62 milligrams per hour. In this study, the replacement of the gas cap and the washer of the fuel tank were regarded as measures to reduce the amount of evaporated fumes [5]. It is important to point out that the Iranian and international standard level of benzene in ambient air is 1.56 ppb and in advanced countries like Japan is 0.69

ppb. For most countries in the world, the Euro 4 standard was used in 2005[6].

The laboratory tests indicate that longtime exposure to benzene has destructive effects on the blood cells, especially the bone-marrow cells. These effects cause the reduction in production of bone-marrow cells and anemia. The long term effect of benzene is leukemia. Environment Protection Agency (EPA) categorizes benzene in group A of carcinogenic substances. Also, the International Agency for Research on Cancer (IARC) refers to benzene as a carcinogenic substance for humans[7-9].

2. Material and Methods

In this research, the benzene concentration is measured by PhoCheck EX5000 equipment. This device is portable and with the aid of Photo Ionization Detector (PID) mechanism can measure the benzene concentration level with high precision (± 1 ppb). The PhoCheck takes samples from the gasoline fumes with the flow rate of 220 millimeters per minute. This device with its high precision (ppb level) samples the benzene through a portable laboratory chromatograph. It is important to point out that Krypton lamp of 10.6 eV is used in this device. One of the most important advantages of this equipment is its approved technology to determine the benzene concentration with the accuracy of 1 ppb to 10000 ppm as well as its good performance in weathers ranging from -20 to 60 degrees[10].

In this study, 350 automobiles encompassing 20 models are examined in the Automobile Technical Inspection Center of Tehran. The benzene concentration due to the gasoline fume is measured at three important spots namely, the gas cap, muffler and inside the cabin during a period of 5 to 10 minutes (for each car). It

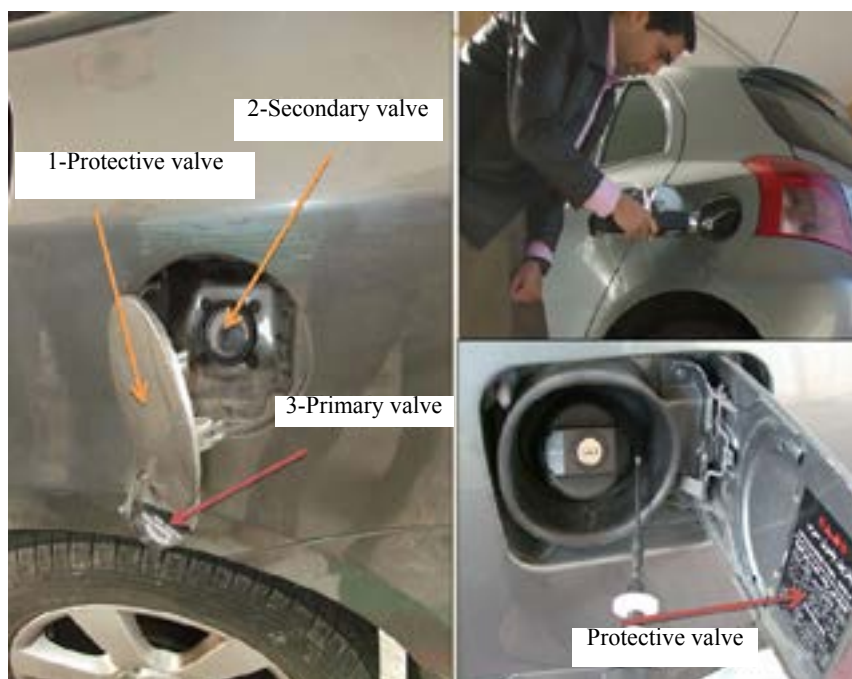


Fig. 1. Sampling method of the fuel tank, the protective valve, primary and secondary valves (if present)

is important to point out that all the cars were tested for the fume emission, after they received their certificate from the Technical Inspection Center. All the Iranian made cars are required to be inspected annually after the 2nd years of production and obtain the certificate. For the ease of study, 350 automobiles were divided into two categories' of imported and domestic vehicles.

In most of the studied cars, there were three protective valves for the gas cap (except the Peugeot 206). The protective valve has a physical function without being in direct contact with the gasoline and its fumes. However, if the first valve

(which is in direct contact with the gasoline and the fumes) fails, the leaked fumes would enter the small chamber of the protective valve for subsequent release to the atmosphere.

The second valve plays its role in controlling the fumes and the overflow of gasoline. In most of the domestically manufactured cars (except Renault L90), this valve does not exist. Figure1 illustrates the position of the three valves and the means to measure benzene. During measurement, the engine is off and only the protective valve is open. Since the valve in Peugeot 206 is in one piece, only the space between the chassis and the gas cap is sampled. Unfortunately, in Peugeot 405 with carburetor, the

Table 1. The minimum, maximum and average concentration levels of benzene in 12 models of imported cars (the amounts are in ppb)

Car Type	Hyundai	Nissan	Mazda	Gol	Kia	Zantia	Roniz	Cielo	Toyota	Prado	Benz	BMW
Average	0.03	0.98	0.21	0.86	0.16	0.34	2.34	0.57	0.68	0.12	0.15	0.1
Max	0.397	3.6	0.83	9.4	0.98	0.97	6.9	2.3	4.3	0.3	0.73	0.7
Min	0	0	0	0.82	0	0	0	0	0	0	0	0

Table 2. The minimum, maximum and average concentration of benzene in domestic vehicles in 8 models (measured in ppb)

Car Type	Tondar 90	Paykan	Pars	405	206	Pride	Samand	Rio
Average	6.59	76.21	26.21	6.83	3.09	43.86	3.94	0.43
Max	38.2	296	151	59.6	51.5	295	7.35	1.95
Min	0	2.06	0	0	0	0	0	0

gasoline fume was emitted from other parts of the car (underneath the fuel tank and the engine).

3. Results and Discussion

3.1. concentration levels of benzene in 12 models of imported cars

The imported automobiles consisted of 116 vehicles from 12 company models. The results indicated that Gol (manufactured by Volkswagen) has the highest amount of benzene leakage from the gas cap. The average concentration of benzene in this group is 86.5 ppb. The lowest concentrations of benzene were detected in Hyundai, Kia, Mercedes Benz, BMW and Prado in amounts of 0.03 ppb, 0.16 ppb, 0.15 ppb, 0.01 ppb and 0.12 ppb, respectively. It is important to point out that Mercedes Benz and BMW models in 70 percent of the cases registered zero concentrations (the best condition). With respect to the fuel type (super and regular gasoline), 28 percent of the samples used were super unleaded gasoline (Octane number of 95) and 72 percent were regular unleaded gasoline (Octane number of 87). The average age of the vehicles in this classification was 3.8 years. About 65 percent of the sampled automobiles had less than 3 years of operation.

In Table (1), the minimum, maximum and average concentrations of benzene are provided. The minimum amounts of measured benzene in all models, except Gol, were zero. Gol model showed

the highest benzene leakage from the gas tank.

It is important to point out that the most important reasons for the emission of benzene fumes in this category are lack of tightening the gas cap and over fueling (pumping too much gasoline into the fuel tank). The average concentration of emitted benzene from the fuel tank of the imported vehicles (116 automobiles) is 0.96 ppb.

3.2. concentration levels of benzene in 8 models of domestic vehicles

In the domestically manufactured auto category, a total of 234 cars in eight various models are investigated. Based on the results, Paykan and Pride show the highest leakage of benzene from the gas cap with the average benzene concentrations of 21.76 and 86.43 ppb, respectively. It should be pointed out that the average age of the examined automobiles was 4.8 years, where 65% of the sampled cars had less than 5 years of age. In regard to the fuel type consumption, the super and regular gasoline was used 22.2% and 77.8%, respectively. The lowest concentrations of benzene are detected in Rio and Peugeot 206 as 0.43 and 3.09 ppb, respectively. It is important to mention that Peugeot 206 has registered zero concentration in over 35% of its samples. Table 2 presents the minimum, maximum and average benzene concentration.

It reveals that the minimum benzene concentration in all models except Paykan was zero. The primary

reasons for the emission of benzene fumes in this group are technical defects of the primary gas cap, lack of the secondary gas cap, over fueling and lack of canister system. Also, about 9% of the domesticated vehicles run on carburetors whose average benzene concentration (in 234 automobiles) is 20.89 ppb. As it is shown in Table 2-2, the emission from the gas caps goes up as the age of the vehicle increases.

4. Conclusions

Majority of the domestic cars emit high levels of benzene from the gas cap, muffler and the gas tank. The best and worst domestically manufactured automobiles are Peugeot 206 and Pride, respectively. The most prominent reasons for high concentration of benzene in this category are the lack of appropriate catalyst system, technical defects in fuel system, and fuel leakage from the gas cap. Amongst the imported car category, Kia and Hyundai groups have the lowest emission of benzene. In most of the imported cars, the amount of benzene in the three measured areas was negligible. This is due to the use of new technology and adaptation of strict environmental standards by the manufacturing country.

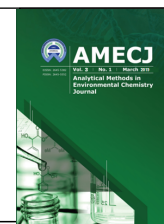
Based on the research results, the amount of benzene concentration due to the leakage of gasoline fumes from the gas cap in domestic cars is approximately ten times higher than the imported cars. In Pride models, the level of gasoline fume emission is considerable and the benzene concentration is 15 times higher than Peugeot 206. Moreover, the average benzene concentration from the emission of gasoline fumes from the gas cap of the imported cars is less than 6 ppb. However, this number for much of domestic cars was higher than 6 ppb. Pride

is identified as the most polluting vehicle in the domestic car category. The research results indicate that the annual inspect of the gas tank, periodical replacement of washer, and modification of the gas cap system in the domestic cars have significant impact on the reduction of gasoline fumes.

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Environmental Health: Evaluation of heavy metals pollution in Isfahan industrial zone from soils, well / eluent waters and waste water by microwave- electro-thermal atomic absorption spectrometry

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ABSTRACT

In this study, soils, well waters, drinking waters, and waste water in the Isfahan industrial area were sampled in spring and summer 2018. In 8 points of industrial zone, important toxic heavy metals such as, lead (Pb), Cobalt (Co), Nickel (Ni), Chromium (Cr), and Cadmium (Cd) were sampled from surface soil (up to 2 m), well/drinking waters and waste water. After sample preparation with micro-wave digestion technique, the concentration of heavy metals was determined by electro-thermal atomic absorption spectrometry (ET-AAS). According to the well water analysis, the mean concentration of Cr, Ni, Co, Cd, and Pb in well water were 95 $\mu\text{g L}^{-1}$, 146 $\mu\text{g L}^{-1}$, 185 $\mu\text{g L}^{-1}$, 12 $\mu\text{g L}^{-1}$, and 11 $\mu\text{g L}^{-1}$, respectively. In well water, the concentrations of Cd, Ni, Cr and Co were found much higher than Pb in comparison with the references of World Health Organization (WHO). Also, the concentrations of such elements in soils and drinking waters are less and near found in accordance to EPA and WHO references respectively. In addition, the concentration of metals in waste water of industrial area was more than well waters. Therefore, the pollution of heavy metals such as Cr, Co, Cd, and Ni in wastewaters of industries can be diffused to well waters and eluent waters in this region and cause many problems in plants and humans.

Keywords:

Heavy Metals

Environmental Pollution

Waters and Soils

Electro-thermal Atomic

Absorption Spectrometry

1. Introduction

Heavy metals are a group of elements with a mass density greater than 4.5 g cm^{-3} , which tend to release electrons in chemical reactions and form simple cations. Heavy metals such as, Cd, Ni, Co, Cr, and Pb is potentially toxic; in addition, their effects in water, plants, and soil are very important. Prolonged accumulation of heavy metals through food stuff may lead to chronic effect in the nerve system, kidney and liver of humans [1-4]. The sources of anthropogenic contamination or pollution of the

environment by heavy metals include different branches of industry, the power industry, transport, municipal waste management, waste dumping sites, fertilizers and waste used to fertilize soil. The heavy metals from these sources are dispersed in the environment and they contaminate soil and water. They also (directly or indirectly through plants) get into human and animal bodies. After entering heavy metals from water or soil to vegetables these metals can enter people's diet and consequently exert their effects. Soil chemical composition plays important role in composition of plant materials. Overall toxic metal availability in soil contributes to metal contents in vegetables. Soil eco-system throughout

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world has been contaminated with heavy metals by various human activities and movement of metals in food chain has become human health hazard [5, 6]. Nickel does not bio-accumulate to a great extent in animals. There is evidence of uptake and accumulation in certain plants. Nickel food intake in the United States ranges is between 69 and 162 μg per day for adults. The standard of United Nations Food for irrigation water is 200 $\mu\text{g L}^{-1}$. The US EPA primary drinking water standard is 0.1 mg L^{-1} [7]. The trace amount of nickel and cobalt, are indicated to be either necessary or toxic depending on their environment concentration range. For example, due to studies on chicks and rats, nickel is apparently essential for proper liver function, or cobalt is at the core of a vitamin B12. On the other hand, some of nickel and cobalt compounds are carcinogenic [8–10]. Lead is a common industrial toxin and environmental pollutant and can enter the human body. It can affect the nervous system significantly, especially on the central nervous system. Industrial development has paid attention to the adverse effects of lead pollution on people's health [11]. A series of literatures also showed that even if children's blood lead levels below 10 $\mu\text{g dL}^{-1}$, they can appear significant neurological dysfunction. Some researchers showed that many rivers had lost its self-purification capacity because of receiving so many industrial wastewaters [12–14]. Cadmium is highly toxic and has been implicated in some cases of poisoning through food. Minute quantities of cadmium are suspected of being responsible for adverse changes in arteries of human kidneys. The FAO-recommended maximum level for cadmium for irrigation water is 10 $\mu\text{g L}^{-1}$. USEPA drinking water standard for cadmium is 0.005 mg L^{-1} [15]. Chromium can enter the human body through breathing, food and drinking water. Chromium salts are used extensively in industrial processes and may enter a water supply through the discharge of wastes. Chromium may exist in water supplies in both the hexavalent and the trivalent state although the trivalent form rarely occurs in potable water. USEPA drinking water standard for chromium and FAO recommended the maximum

limit for irrigation water as 100 $\mu\text{g L}^{-1}$ [16]. The World Health Organization (WHO) states that the guideline values of 50 $\mu\text{g.L}^{-1}$ Cr (VI) are considered to be too high as compared to its Geno toxicity [17–19]. Thus it is obvious that determination of heavy metals, at trace level, in water and environmental samples is of great significance from the public health and environmental point of view. Wastewater irrigation has been practiced widespread in the world [20, 21]. Wastewater irrigation creates both opportunities and problems in agricultural source [22]. It provides important water resources and has the beneficial aspects of adding valuable plant nutrients and organic matter to soil [23]. However, excessive accumulation of heavy metals in agricultural soil through wastewater irrigation may not only result in soil contamination, but also affect food quality and safety [24]. It is necessary and important to develop sensitive methods for determining heavy metals in soil, and water samples and then, the results must be compared with World Health Organization (WHO) and Environmental Protection Agency (EPA) [25, 26]. Various techniques such as, inductively coupled plasma mass spectrometry [27,28], flame atomic absorption spectrometry (F-AAS) [29], electro-thermal atomic absorption spectrometry (ET-AAS) [30,31] and cold vapor atomic absorption spectrometry(CV-AAS) [32] have been applied for the determination of soil and water samples.

The aim of this study was to monitor the toxic heavy metals such as, Cd, Cr, Ni, Co, and Pb in well waters, drinking waters, waste waters and soils in Isfahan's industrial regions and evaluation of environmental pollution in this area. After microwave digestion of samples the concentration of heavy metals were determined by ET-AAS. The results of data were analyzed using SPSS statistical programmer, PHSTAT, and excel computer packages.

2. Experimental procedure

2.1. Apparatus and materials

Determination of heavy metals (Cd, Cr, Ni, Co, Pb) was performed with a spectra GBC electro-thermal atomic absorption spectrometer (Plus

Table 1. The instrumental conditions of ET-AAS for determination heavy metals.

Element	Cd	Co	Cr	Ni	Pb
Lamp current (mA)	4	7	7	4	5
Wave length (nm)	228.8	240.7	357.9	232.0	217.0
Slit width (nm)	0.5	0.2	0.2	0.2	1.0
LOD ($\mu\text{g L}^{-1}$)	0.05	0.6	0.1	0.8	0.25
LOQ($\mu\text{g L}^{-1}$)	0.2	3	1	5	3
Working range	0.2-1.8	3-45	1-16	5-65	3-40

932, Australia) using a graphite furnace module (GF3000, GBC). The operating parameters for the metal of interest were set as recommended by the manufacturer. All samples in ET-AAS were performed using 20 μL of samples. The pH values of the solutions were measured by a digital pH meter (Metrohm 744). Microwave digestions were carried out with a Multi-wave 3000 (Anton Paar, 100 mL, 20 bar; Austria). The instrumental and temperature programming for the graphite atomizer are listed in Table 1 and 2. All reagents were of ultra-trace analytical grade from Merck Germany. Cd, Cr, Ni, Co and Pb stock solution was prepared from an appropriate amount of the nitrate salt of this analyte as 1000 mg L^{-1} solution in 0.01 mol L^{-1} HNO_3 (Merck). Standard solutions were prepared daily by dilution of the stock solution. Ultrapure water (18 $\text{M}\Omega\cdot\text{cm}$) was obtained from Millipore Continental Water System (Bedford, USA).

2.2. Sampling

In this study, Cr, Co, Ni, Cd and Pb of soil, well water and drinking in eight different location of Isfahan industrial area were evaluated. For sampling, all glass tubes were washed with a 1 mol L^{-1} HNO_3 solution for at least 24h and thoroughly rinsed 8times with ultrapure water before use. As determination of heavy metals concentration in soil samples are very difficult, even contamination at any stage of sampling, sample storage and handling or analysis has the potential to affect the accuracy of the results. All samples prepared in the vicinity of Isfahan industries. Soil and water were sampled from eight points of Isfahan's industrial zone. All of samples prepared from south of Isfahan province (4*4 km^2) (Fig.1). Due to large study area Global Positioning System (GPS) was used to determine the actual coordinates of the sampling sites and to reconfirm the location of the sampling site during subsequent sampling periods.

**Fig 1.** Sampling water and soil in the Isfahan oil refinery area, and G point is oil refinery.

Table 2. temperature programming for the graphite atomizer of ET-AAS

Element	Cd	Co	Cr	Ni	Pb
Drying	130	130	130	130	130
Ashing	300	800	1100	900	400
Atomization	1800	2300	2500	2400	2000

In preliminary studies soil and water investigation consists of eight locations, in order to determine and to provide ground information for subsequent detailed planning of the future work. For soil sampling multiple sub samples were taken from each location and then samples were homogenized into composite sample with stainless spoon and then sub sampled by spoon into each sample container to get accurate results.

2.3. General procedure

Five samples of well/drinking water(16×5), wastewaters (10) and soil(8×5) were collected from eight Isfahan's industrial region (N=130). Samples were placed in polyethylene bags and brought to laboratory of IPIHR for analysis. All samples were washed with tap water followed with DDW (double de-ionized distil water). In the laboratory, the soil samples after air drying at room temperature were sieved with nylon mesh (2 mm). The <2 mm fraction was grinded in an agate and pestle and passed through a 63 micron sieve. Selected physio-chemical properties of these soils were analyzed using standard methods. Soil pH was measured in suspension of soil to water ratio (1:2) using calibrated pH meter. Briefly, 1 g of the soil sample was placed in a decomposition polyethylene tube to which was added 1 mL of 10 % (w/w) H₂O₂ and 7 mL HNO₃ concentrate. The mixture was digested by heating and irradiating for 60 min by microwave digestion system (MDS). After heating the sample at 120 °C the volume of the digested sample was set to 0.5 mL and dilution up to 3 mL

with DDW. Following the instruction of Instrument operational manual provided by manufacturer, analysis of Ni, Co, Cd, Cr, and Pb was carried out using atomic absorption spectrophotometer coupled with graphite furnace assembly. The blank solutions proceeded the same way and are used for the preparation of the calibration solutions and for measurement of the blanks. Soil samples were prepared in 3 depth of surface earth (5 cm, 50 cm, and 100 cm). In order to quantitating analyze and confirm the relationship among soil properties and heavy metal content, the correlation analysis was applied to dataset.

3. Results and discussion

The results of determination of heavy metals in Isfahan's industries regions show that the concentration of Cr, Co, Ni, Cd and Pb in drinking water and soil were very low and did not exceed the permissible levels (TLV). In soil samples, all of heavy metals (Cr, Co, Ni, Cd, Pb) have low concentration in accordance to EPA and WHO references. In addition, soil samples collected from the land irrigated with waste water were higher than well water . Heavy metals accumulated in the surface soil layer may migrate into the deeper layers, and consequently pose a threat of well water contamination. The parameters of pollutants depend on the type of soil and its properties. The mean of concentration of Ni, Co and Cd in surface soil (5.23 ± 0.22 , 8.42 ± 0.42 , 0.35 ± 0.02) were higher than deeper layers (2.15 ± 0.12 , 3.28 ± 0.19 , 0.08 ± 0.01), but Pb and Cr were uniform in surface and

Table 3. Permissible limits of the metals in soil and water (FAO/WHO)

WHO	Ni	Co	Cr	Cd	Pb
Soil ^a	2-40	0.1-50	1-180	0-0.2	1-200
Water ^b	70.0	80.0	50.0	3.0	10.0

^a $\mu\text{g g}^{-1}$

^b $\mu\text{g L}^{-1}$

Table 4. Mean concentration of metals in soil and water of Isfahan's oil refinery regions (N=10)

Sample	Average Metal		Concentration ^a		
	Cr	Ni	Co	Cd	Pb
Waste Water ^b	95.24± 4.31	146.48± 7.12	185.48± 9.03	23.36 ± 1.33	11.64± 0.53
Well water ^b	28.35 ± 1.48	52.12 ± 1.86	68.53 ± 2.77	0.26 ± 0.01	1.08 ± 0.04
Soil ^c	3.38 ± 0.17	3.47 ± 0.18	5.17 ± 0.28	0.13±0.006	2.19 ± 0.14

^a Mean of three determinations ± confidence interval (P = 0.95, n=5)^b µg L⁻¹^c µg g⁻¹

Sample	Average Metal		Concentration ^a		
	Cr	Ni	Co	Cd	Pb
Wastewater ^a	377.3± 14.4	246.3± 11.8	299.7± 12.3	67.5 ± 4.2	94.1± 6.5

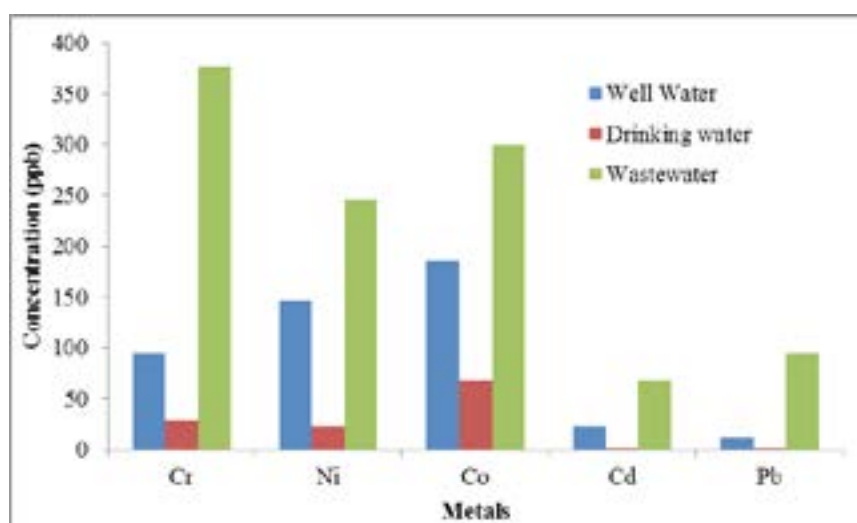
^a µg L⁻¹

deeper layers of soil. Concentrations of Cr, Co, Cd and Ni in waste water near industrial region (were higher than well water and lead was not significant effect (P<0.05). The dietary limit of metals in water and soil is very important and permissible limits of the metals in soil and water have reported by FAO/WHO [20-24] (Table 3). Mean concentration of Ni, Co, Cr, Cd and Pb in soil, well/drinking water obtained in Table 4.

Many industries located near agricultural land in Isfahan's regions. Some of points (A, B) was near to industries regions have higher concentration of heavy metals than other points (C-H). Nickel is a toxic metal that occurs naturally in environment. Results of our study show that maximum

concentration of nickel was found in waste water (246.32 µg L⁻¹) and the minimum concentration in well water and drinking water were obtained 37.43 µg L⁻¹ and 8.26 µg L⁻¹.

The mean concentration of nickel in drinking water, well water and soil were 22.12 ± 1.86 µg L⁻¹, 146.48±7.12 µg L⁻¹ and 3.47 ± 0.18 µg g⁻¹, respectively. Cobalt is an essential micronutrient for man, animals, and plants for a range of metabolic process. However, in any case the use of cobalt supplementation has been associated with toxic side effects such as cardiomyopathy. The high concentration of cobalt in human as compare to the maximum permissible limits (0.01 µg g⁻¹) can be affected on nervous system, bones, liver,

**Fig. 2.** Mean concentration of metals in well, drinking and waste water of Isfahan's industries regions.

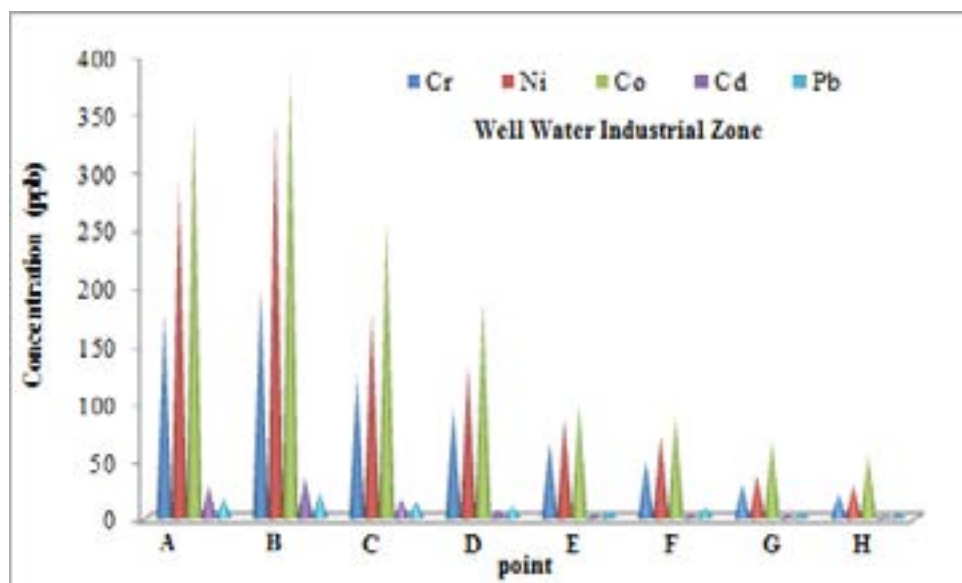


Fig. 3. Mean concentration of metals in sampling point of waste water in Isfahan's oil refinery regions.

pancreases, teeth and causes blood diseases. Results of our study show that maximum concentration of cobalt was found in waste water ($357.7 \mu\text{g L}^{-1}$) and the minimum concentration in well water and soil ($32.12 \mu\text{g L}^{-1}$, $0.38 \pm 0.01 \mu\text{g g}^{-1}$). The mean concentration of cobalt in well water, waste water and soil were $185.48 \pm 9.03 \mu\text{g L}^{-1}$, $299.7 \pm 12.3 \mu\text{g L}^{-1}$ and $5.17 \pm 0.28 \mu\text{g g}^{-1}$ respectively. Cobalt and nickel have a high concentration in waste water as compared with WHO references. USEPA drinking water standard for chromium and FAO recommended the maximum limit for irrigation water as $100 \mu\text{g L}^{-1}$. Results of chromium show that maximum concentration was found in waste water ($483.53 \mu\text{g L}^{-1}$) and the minimum concentration in well water and soil ($17.09 \mu\text{g L}^{-1}$, $1.08 \pm 0.07 \mu\text{g g}^{-1}$). The mean concentration of Cr in well water, waste water and soil were $95.24 \pm 4.31 \mu\text{g L}^{-1}$, $377.3 \pm 14.4 \mu\text{g L}^{-1}$ and $3.38 \pm 0.17 \mu\text{g g}^{-1}$, respectively. Speciation chromium in waste water showed that the Cr (VI) has high concentration than Cr (III) ($C < 65\%$) and in well water had more less 10%. Cadmium and lead have a high concentration in waste water as compared with WHO references. In waste water, maximum / minimum concentration of Cd and Pb were found ($91.3 \pm 5.3 \mu\text{g L}^{-1}$ / $24.4 \pm 1.9 \mu\text{g L}^{-1}$) and ($135.7 \pm 7.2 \mu\text{g L}^{-1}$ / 36.5 ± 2.2

$\mu\text{g L}^{-1}$), respectively. The mean of Cd and Pb in well waters, drinking waters and wastewaters was achieved (12.37 ± 1.33 ; 0.26 ± 0.01 ; 67.5 ± 4.2) and (11.64 ± 0.53 ; 1.08 ± 0.04 ; 94.1 ± 6.5), respectively.

4. Conclusion

In this study, the concentration of heavy metals such as Cr, Co, Cd, Pb, and Ni in soil, well water and waste water in Isfahan's industries regions were analyzed. After digestion the soil and waste water samples with microwave, the concentration of heavy metals determined by ET-AAS. The concentrations of Cr, Co, Cd, Pb and Ni in drinking water and soil have low TLV with compared to WHO/FAO references. But the same metals except lead have high concentration in well water. Lead concentration was not significant in samples ($P < 0.05$). Figure 1 showed that the A,B points have higher concentration of heavy metals than other points in Isfahan's regions. The mean concentration of Cr, Ni, Co, Cd, and Pb in well water were 95.24 ± 4.31 , 146.48 ± 7.12 , 185.48 ± 9.03 , 12.37 ± 1.33 , and 11.64 ± 0.53 , respectively. Therefore, Cr, Co, Cd, and Ni in well water from these regions can probability cause pollution in environmental and humans. In addition, the concentrations of such elements in soils and well/drinking waters are less

and near found in accordance to EPA and WHO references, respectively. Therefore, the pollution of heavy metals such as; Cr, Co, Cd and Ni in Isfahan industrial regions can be diffused to well waters and eluent waters and cause many problems in plants and humans.

5. Nomenclature

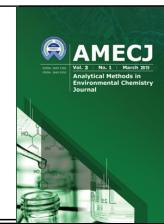
DDW: double de-ionized distil water

WHO: Water Health Organization

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Synthesis and performance of graphene and activated carbon composite for absorption of three-valence arsenic from wastewater

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ABSTRACT

The presence of high levels of arsenic in the effluent is a major concern of human, and the removal of it from the wastewater is hard and costly. The most common techniques for removal of arsenic are membrane separation, ion exchange, oxidation, and coagulation. All of these technologies eventually lead to the separation of arsenic from wastewater and its accumulation among absorbent materials, which are precipitated as sludge or extracted from liquid intermediate phase. In this adsorption method, materials such as active alumina, active carbon, titanium oxide, silicon oxide, and many natural and artificial elements are used. Considering that active carbon is used as the most common arsenic adsorbent in wastewater treatment processes, this study has been considered as the main adsorbent and attempted to improve its surface properties by graphene nanosheets. Thus, by adding 4.5 w.% graphene to the carbon structure, its porosity increases, and the ion exchange behavior and surface load are corrected. In this research, the effects of time process, concentration of arsenic, and adsorbent are evaluated in different pH values. It has been observed that the maximum adsorption of arsenic is 91.8%; in addition, when graphene is used, the rate of absorption of Arsenic has increased about 5.2%, and the process time is shortened. In addition, using graphene is cost-effective. It is also observed that the efficiency of the adsorption process increases near neutral pH values; therefore, the adsorption method by graphene/activated carbon composite in neutral cells can be used as an additional method for industrial wastewater treatment.

Keywords:

Arsenic

Graphene

Activated carbon

Adsorption

Acidity of wastewater

1- Introduction

Nowadays, five major and hazardous pollutants which can pollute and threaten drinking water, groundwater, urban water, and bottled water are known. The pollutants are arsenic, lead, fluoride, chromium, and radioactive substances. Due to the impossibility of biodegradation of arsenic in the environment, it remains in contaminated water, and thereby, it is considered as one of the most

hazardous pollutants in wastewaters and water resources. In addition, the tendency of arsenic to accumulate in the members of the body causes dangerous diseases and cancers. The effects of arsenic on the liver and nervous networks are very prominent and cause a delay in mental activity and anemia. In addition, arsenic enters in the water, irrigated water, and environment in various ways such as mining, printing, and reproduction industries, petrochemical complexes, and chemical industries or as a pollutant in their effluent. According to available standards for drinking water, the limit for arsenic is up to 10 ppm

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[1]. There are various methods for the adsorption or removal of arsenic from contaminated water sources, the most important of which are chemical deposition [2], reduction by electron ultrafiltration [3], ion exchange [4], and absorption process [5]. Among these approaches, the absorption method is more cost-effective, efficient, and easy-to-absorb, and extensive studies on the absorption of arsenic by adsorption processes have been reported [7-5]. However, researches are looking for adsorbents with a higher absorption rate, the identification of an ideal adsorbent for the maximum absorption of arsenic has not yet been suggested clearly. Activated carbon has been used with the proper properties as an efficient absorbent in treatment of industrial wastewater for a Long time, especially in the absorption of metal ions. In the meantime, various technologies, including nanotechnology, have increased the capacity of adsorbents used to absorb more pollutants, including arsenic, so that a new view has been opened in the field of wastewater treatment. For example, carbon nanotubes [8], graphene [9], graphene-oxide [10], various graphene base materials, including graphene hybrids [11] and graphene/metal oxide nanocomposites [12], including nano-absorbents which have been used in extensive researches, and by using them, the best results have been obtained. Moreover, no information is available to use the adsorption of graphene/activated carbon for removing arsenic from wastewaters. Graphene oxide has shown good results in the removal of some heavy metals from the effluent, which, in its structure, oxygen acts as an absorption agent for metal ions [13]. In graphene/activated carbon composite, each of graphene and activated carbon structures exhibits distinct effects on each other's performance. For example by considering the effect of activated carbon on graphene behavior, it can be admitted that the layer of graphene plate is rolled onto activated carbon that not only prevents the graphene from sticking together, but also increases the porosity of the composite structure. Consequently, it increases the specific surface of adsorbents, which it is ideal target for sorbents.

On the other hand, graphene sheets, due to their very small structures, act as a filler among the active carbon structures and due to its conductive behavior, and thereby, the absorption path in the new structure of activated carbon is shortened. It also facilitates the transfer of free electrons in the composite structure and lowers its resistance. This phenomenon is also the ideal goal of an ideal adsorbent in sorption of ions [14]. In this research, the graphene/activated carbon composite synthesized as a porous adsorbent with a high specific surface area is used for absorbing arsenic from industrial effluent.

2. Experimental

2.1. Synthesis of Activated carbon/graphene composite absorbent

At First, graphene oxide has been obtained by Hammers method with the mechanism of opening of graphite layer sheets. After that, a double layer dish with dilute sulfuric acid is washed, and while the solution of sulfuric acid including graphite is stirred, the temperature of the solution is reached to 0 °C using liquid cooling circulator. The amount of 2300 ml of sulfuric acid (98%) has been poured into the reactor and mixed with 100 g of pure graphite powder into the container, and the mixing operation has been carried out for 30 minutes. Afterwards, the amount of 300 g of solid potassium permanganate powder is slowly added to the mixture during 6 hours, and the mixture is stirred for one hour after completion. Then the temperature circulator is increased to 40 °C, and after stabilizing the temperature, the mixing operation continuous for about three hours. For dilution, 500 ml of distilled water is added with caution to the reactor, and the circulator bleach and 3.5 liters of distilled water are poured into a larger container, and then the contents of the reactor are slowly transferred to a larger container. Afterwards, the mixing operation is carried out for one hour. The amount of 300 ml hydrogen peroxide 30% has been slowly added to the container, then mixing condition has continued for 2 hours. Then 3 liters of chloride acid have been added to 3 liters of distilled water separately.

Afterwards, the produced solution has been added to the contents of the container. Then the process continues for one hour. The stirrer has been turned off, and the mixture has been subjected to the intense ultrasound waves for 4 hours since the opened plates do not adhere to each other. After that, the container has been settled about eight hours until the sediment is formed. Then from the above part of the container, the produced solution has been poured out, and the sediment contents of the container are filtered. The strained cake is transferred to a Chinese plant. Afterwards, the cake is placed in a vacuum oven at 50 °C for two hours, and then rinsed ultrasonically with distilled water until neutral pH is achieved. After the neutralization process, the powder formed is used as the graphene oxide [15]. To prepare activated carbon, first 200 g of powdered glucose is placed into a quartz tube. The reactor is placed under nitrogen atmosphere for 30 minutes. It is then gently warmed up to a temperature of 350 °C and remained for 2 hours. The glucose is carbonized under these conditions and is colored as a black powder. In order to increase the activated carbon efficiency, its surface activation is carried out to perform a graphene composite synthesis reaction under a two-step pre-activation process. In the first step, at first, 10 g of activated carbon powder is mixed with 20 g of zinc chloride, and the mixed composite powder is added to 300 ml of distilled water in a closed container. Afterwards, the produced solution is exposed to heat for 7 hours at 70 °C. During the heating process, the water must not evaporate, and the process is carried out in a dilute aqueous medium. This action causes the activated carbon to become more porous. Then, the mixture becomes smooth with a filter paper, and the smooth mixture is dried in an oven at 80 °C for 1 hour. The dried powder is placed in a tubular quartz reactor, and the powder is heated for one hour under neutral atmosphere while temperature is equal to 400 °C. The powder has been extracted from the reactor. Then the powder has been poured into a one-molar chloride acid at 90 °C for 30 minutes. This has been carried out to remove chloride from the remaining activated

carbon powder. The remaining mixture is filtered and washed with warm distilled water several times to remove remaining and additional chemicals. The filter cake is dried in an oven at 65 °C for 11 hours. In the second step, 10 g of the carbon powder obtained from the first step has been mixed with 30 g of potassium hydroxide, and the obtained mixture has been placed in 300 ml of distilled water into the container and brought to a temperature of 50 °C. Then the mixture is mixed with alternating heat for 1 hour. The resulting mixture has been filtered with filter paper. Afterwards, the filtered mixture has been dried in an oven that its temperature is equal to 80 °C for 1 hour. The dried powder is placed in a tube quartz reactor and heated slowly at 700 °C for one hour under neutral atmospheres. The powder has been brought out from the reactor. Afterwards, it has been dried in an oven at 40 °C for one night. Dried powder is a porous activated carbon that is susceptible to participation in the graphene composite structure. In order to synthesize the active graphene / activated carbon composite, first add 0.9 grams of dried graphene powder to 200 ml distilled water and add ultrasonic waves of 100 watts for a period of two hours, which appears as a mixed mustard mixture. Then, the amount of 20 grams of activated carbon powder is slowly added to the ultrasonic mixture for 3 hours. The mixture is placed at 50 °C for one day, and then the water evaporates. The remaining solids are introduced into a quartz reactor formed in a tube, and under a nitrogen atmosphere, it is slowly heated to 350 °C and left for 2 hours. The final product of this reactor is the graphene/activated carbon composite [16].

2.2. Study of structural properties of graphene/activated carbon composite

In order to investigate the crystalline structure and the phases present in the synthesized graphene/carbon composite, X-ray analysis has been carried out. In this study, a XRD spectrometer (Philips, PW-1840) with a beam of 1.494 nm and a voltage of 40 kV and a current of 30 mA has been used. The spectrum obtained has been compared with

the Hammers graphene XRD. This comparison is shown in Figure 1.

According to Fig. 1 (a), it is seen that the graphene obtained from the Hammer's process at 12.5 degrees has a sharp and narrow peak, which indicates the crystalline structure of the graphene oxide form, this means that the process of opening graphite plates in the reaction of oxidation with concentrated acid (Hammers process) is successfully achieved. While in Figure 1 (b), the peak has been shifted to a point of 26.5 degrees and its intensity is very low. This criterion is a carbon-crystalline structure with double bonds without the presence of oxygenation groups, which has been observed in pure graphene structure. As a result, the process of making the graphene/activated carbon composite, which has undergone a severe

heat stroke, causes the oxygen groups have been removed from the composite structure. It also shows that the synthesized composite structure is free of any non-carbon bonding, in other words, there is no additional contaminant in its structure. In the following, a comparison of the two types of graphite and synthesized composites is made, as seen in Figure 2.

It is observed that the peaks of D and G in the area of cm^{-1} of 1338 and 1611 cm^{-1} appear to be good in this function respectively. The D-peak represents structural defects that appear due to its presence in destructive environments such as concentrated (or strong) acidic environments or the presence of different operating groups on the graphene's structural surface, while the G-peak is due to the graphite crystalline network produced by the carbon bonds. Thus, the ratio of the intensity of the D/G peaks is an indicator of the structural state of graphene, which is equal to 0.88, as shown in Fig. 2a. This ratio indicates the presence of high oxygen groups on the structure of the Hammers graphene, while in Fig. 2b, this value is increased to 1.69 due to the elimination of oxygen's groups of the present graphene in the destructive environment. These results are also consistent with the XRD analysis shown in Fig. 1. In order to study the surface properties of graphene/activated carbon composite, the TEM image has been used, as seen in Fig. 3. According to Fig. 3, it can be seen that the

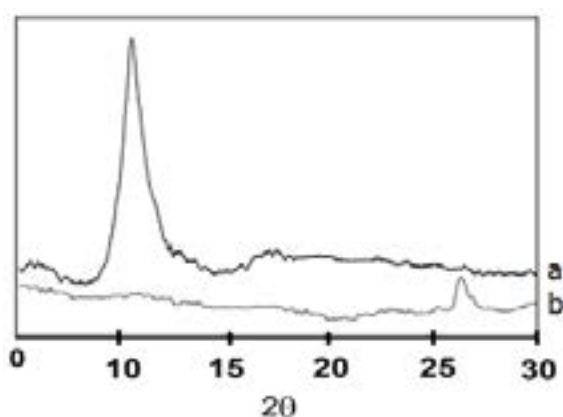


Fig. 1. XRD spectrum of graphene / activated carbon composite

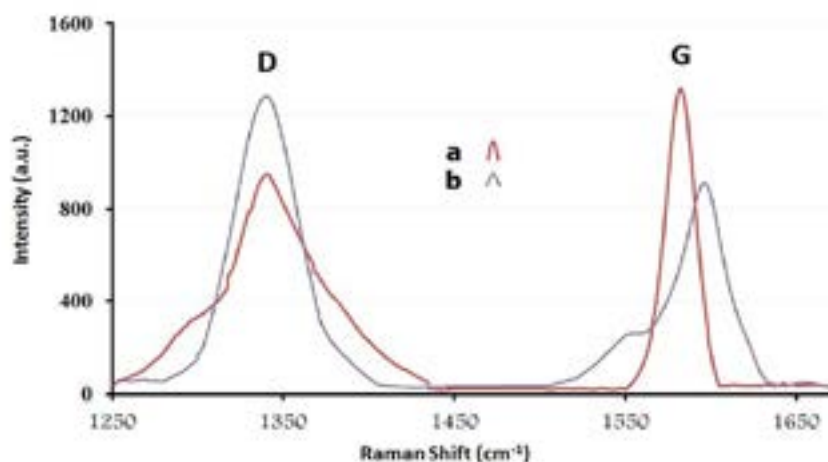


Fig. 2. Raman spectrum: (a) Graphene (b) Graphene / activated carbon composite.

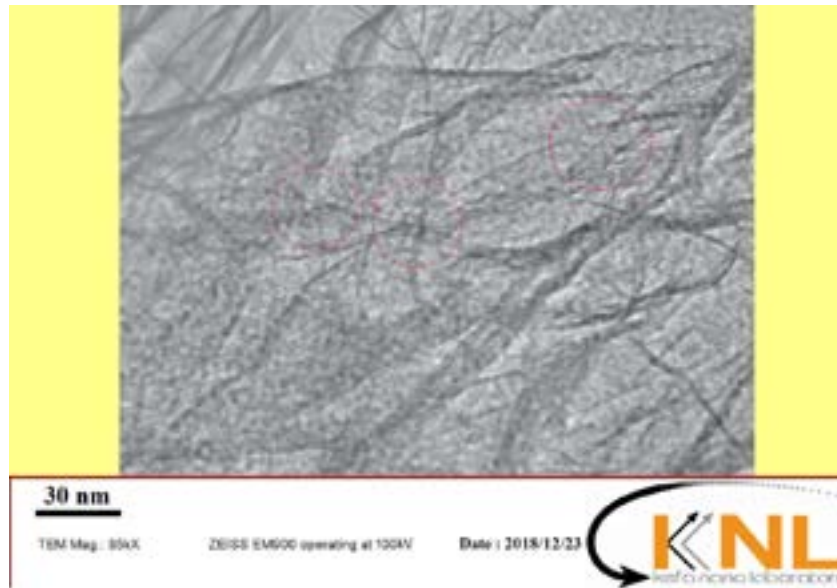


Fig. 3. TEM image of graphene/active carbon composite.

layered structure of graphene nanosheet, which has a micro-length, is well opened, and active carbon particles are interacting. Small graphene layers are randomly and irregularly distributed in activated carbon particles.

Moreover, in circular shapes, in addition to carbon, they also interact with each other, which have created a structural network in activated carbon and produced a total porosity. Moreover, this phenomenon is due to a large amount of disruption in the open graphene layers during the Hammers process which is linked by functional groups in the edges and structural defects of graphene to activated carbon. The very narrow channels created by the graphene plates inside the activated carbon structure cause large structural porosity of the composite to be obtained. To investigate the structural porosity of synthesized composites, the technique of nitrogen absorption and desorption under different relative pressures has been used by the BET method. In this research, the Belsorp mini

II BET device, the Japanese company BelJapan, has been used. Preparation of samples is including drying and degassing, which for this purpose, the specimens should be heated in vacuum at 120 °C for 10 to 15 minutes for removing water vapor, carbon dioxide, or other molecules that may occupy the volume of the material cavities. Then the samples cool down to the liquid temperature of the nitrogen gas. Then the amount of nitrogen gas absorbed by the composite or graphene structure is measured by gradually increasing the relative pressure, and its depletion rate is calculated by decreasing the pressure at a constant temperature of 77 K. It has been observed that in each case, with an increase in relative pressure, the nitrogen uptake has increased, and in the depletion mode, the same initial pattern of absorbed nitrogen volume has been obtained. The summary of the results is presented in Table 1. According to the Table 1, graphene has shown an increase in the specific surface area of activated carbon by 87%. Also, the graphene composite with

Table 1. pores status analysis based on BET analysis results.

Structure	Isotherm absorption type	Specific surface area (m ² / g)	Average pore diameter (nm)	Mesoporous (%)	Total pore volume
Hammers graphene	Type I absorption	61	37.6	30	0.37
Activated carbon	Type II absorption	982	8.2	8	2.45
Graphene composite	Type IV absorption	1841	5.6	9	2.91

a specific surface area of 1841 m²/g exhibits a very active surface structure that is very attractive in the absorption region. In addition, the process of synthesis of graphene composites has increased the volume of activated carbon cavities up to 18%, indicating an increase in the absorption capacity of this structure. However, the size of the cavities is not larger and, as a result, the number of each of them is much larger. The presence of graphene in the active carbon structure reduces the size of the cavities, so that the average diameter of the cavities in the composite is reduced by 22%. In other words, the hypothesis of the interaction between graphene and activated carbon on each other in the composite structure is visible from the point of view of the positive effect of graphene on the active carbon structure and graphene reduces the size of the cavities and increases their number in the activated carbon structure. Based on the results of the structural analysis of synthesized composite, which indicates the proper position of this structure as a sorbent, it is further used to absorb arsenic in water.

2.3. The evaluation system of absorbent performance and process variables

In this study, a batch reactor system has been used in a laboratory scale to carry out the process of adsorption and removal of arsenic in water, the schematic illustration is shown in Fig. 3.



Fig. 4. Schematic of the absorption reactor system.

In accordance with Fig. 4, the system, which has been used, consists of a double-headed reactor of Pyrex with an internal volume of 300 cc, which is an environment for an adsorption reaction. During the absorption process, a circulator has been used to transfer the required temperature and to maintain the flow of the agent into the reactor's second wall. The reactor is equipped with a mechanical agitator system that can control the speed of the stirrer in different periods. At the end of the stirrer rod, two parallel blades, with 2 cm in length, are placed at an angle of 1 cm above the bottom of the reactor, which is made of polymer and neutral, with the aim of mixing the wastewater and the lack of deposition of the adsorbent at the end of the container is used during the absorption process. Also, this system provides an opportunity to study the rate of mixing speed in the absorption process. To provide the required heating, a magnetic stirrer equipped with an electric heater can also be used. Arsenic adsorption process for two active carbon adsorbents and graphene/activated carbon composite for 200 cc wastewater containing three-valence arsenic (As^{3+}) in water at 45 °C with an abrasive stirrer 700 rpm has been carried out, and their results have been compared with each other. These processes have been repeated at different times and at different concentrations of arsenic in water and different concentrations of adsorbent and pH values. These values are presented in Table 2.

3. Results and discussion

According to the variables defined, the arsenic adsorption process is performed by two adsorbents including active carbon and active carbon-graphene composite in two pH values. In these experiments, the amount of adsorbent is used, and the time of the adsorption process with the initial concentration of arsenic in the wastewater is changed in two levels. Upon completion of the test, the amount of arsenic in the wastewater is measured by atomic absorption analysis with the PerkinElmer 2380 machine. The amount of adsorption of arsenic after the adsorption process is calculated by the following equation (Eq. 1).

Table 2. The absorption Process Variables.

Number of variables	Non-dependent variable	Low variation level	High Level of variation
1	concentration of absorbers (mg)	100	200
2	time of adsorption	60	120
3	Amount of absorbent (mg As / L)	100	200
4	pH	3	6

$$q_e = (C_0 - C_e) \cdot V / m \quad (\text{Eq. 1})$$

where q_e is the amount of absorption after reaching the equilibrium state with unit mg/g, C_0 and C_e are the initial and final concentrations of arsenic in the wastewater, which their units are mg/L, obtained by atomic absorption analysis and V is the volume of wastewater used per Liter, and m is the absorbent weight used in grams. Then based on the initial concentration of arsenic in the wastewater, the efficiency of arsenic adsorption is calculated. The absorbent absorption efficiency is obtained using the following equation (Eq. 2):

$$\% \text{ Removal} = (C_0 - C_e) / C_0 \times 100 \quad (\text{Eq. 2})$$

Table 2 summarizes the number and conditions of absorption experiments. For more precision and the possibility of repeatability of the experiments,

each experiment has been repeated three times, and its mean value as absorption efficiency has been calculated and reported. In addition, Table 3 summarizes the results of arsenic adsorption under various laboratory conditions.

According to Table 3, it is generally observed that the adsorption rate in activated carbon/graphene composites is higher than of activated carbon, so that under the same conditions due to the positive effect of graphene on porosity. The total amount of adsorption increased from 6.6% to 9.3%, and the highest amount of arsenic adsorption occurred when using 200 mg graphene/activated carbon composite in 120 minutes for effluent with concentration of 100 mg which is 42.4%. It is observed that increasing the concentration of arsenic in wastewater decreases the amount of absorption due to the presence of more arsenic in the wastewater

Table 3. The Summary of the results of arsenic adsorption under various laboratory conditions

Absorbent type	The amount of adsorbent (mg)	Time of absorption (minute)	Initial concentration (mg As/L)	Absorption Test Conditions	pH=6		pH=3	
					Absorption rate (%)	Secondary concentration (mg As/L)	Absorption rate (%)	Secondary concentration (mg As/L)
Activated carbon	100	60	100	AC1	79.2	79.2	74.4	74.4
			200	AC2	77.1	154.2	74.0	148.0
		120	100	AC3	80.3	80.3	74.2	74.2
			200	AC4	79.7	159.4	76.4	152.8
	200	60	100	AC5	86.4	86.4	80.2	80.2
			200	AC6	85.9	171.8	83.4	166.7
		120	100	AC7	84.5	84.5	78.4	78.4
			200	AC8	86.6	173.2	83.3	166.6
Composite	100	60	100	AC/G1	83.8	83.8	77.6	77.6
			200	AC/G2	82.2	164.4	79.1	158.2
		120	100	AC/G3	85.3	85.3	80.4	80.4
			200	AC/G4	83.1	166.2	79.9	159.8
	200	60	100	AC/G5	91.8	91.8	85.5	85.5
			200	AC/G6	90.7	181.4	87.6	175.2
		120	100	AC/G7	92.4	92.4	86.1	86.1
			200	AC/G8	91.6	183.2	88.5	176.9

and the creation of mass transfer resistance in its transfer to the absorbent level. In this case, by comparing the absorbance value for active carbon, the same phenomenon is observed, as the amount of adsorption decreases by about 2.5%. Therefore, the amount of arsenic adsorption by active carbon with the presence of arsenic in large concentrations is inversely proportional, and it can be used as a supplementary method in adsorption. It can be seen that the presence of graphene in the activated carbon structure due to electron exchange in the sites at the edges and structural defects of graphene humors increases the absorption performance. However, the time of the absorption process does not have any significant effects on it, based on this study, if it is required to absorb less than 1% of arsenic in wastewater by using graphene/activated carbon, the time of absorption must be increased twice. In addition, if it is required to absorb less than 1% of arsenic in wastewater by using activated carbon, the time of absorption must be increased 2.3 times. As a result, graphene has increased the adsorption rate, which has accelerated the absorption process, and has a positive effect on the economy of this process. Therefore, due to the negligible difference and the very little effect of absorption time with the presence of graphene, the absorption time at

60 minutes as an optimal point of the process is suggested. By changing the amount of acidity of the effluent from 6 to 3, the empirical values obtained in Fig. 2 are reported.

According to Fig. 5, it is observed that with increasing pH in all experiments, the amount of adsorption increases. Generally, it is seen that the reduction of the pH of the effluent is strongly influenced by the amount of absorption due to the competition of adsorption of arsenic in the acidic environment. In addition, it is observed that in lower pH values, the amount of adsorption decreases, but the intensity varies in different conditions. When only activated carbon adsorbent is used, the greatest effect of pH is on AC3 adsorption conditions, which changes 6.1% of absorption, whereas when composite adsorbent is used, the most effect of pH is on AC/G7 adsorption conditions, of which 6.3 units change the absorption percentage. In general, the maximum amount of arsenic adsorption decreased by 6.3%, which is related to dilute arsenic concentrations when 200 mg of composite adsorbent is taken at 60 and 120 minutes. Therefore, it is noted that the time of adsorption process has no significant effect on the amount of arsenic adsorption. To better evaluate the effect of time on adsorption, absorption processes

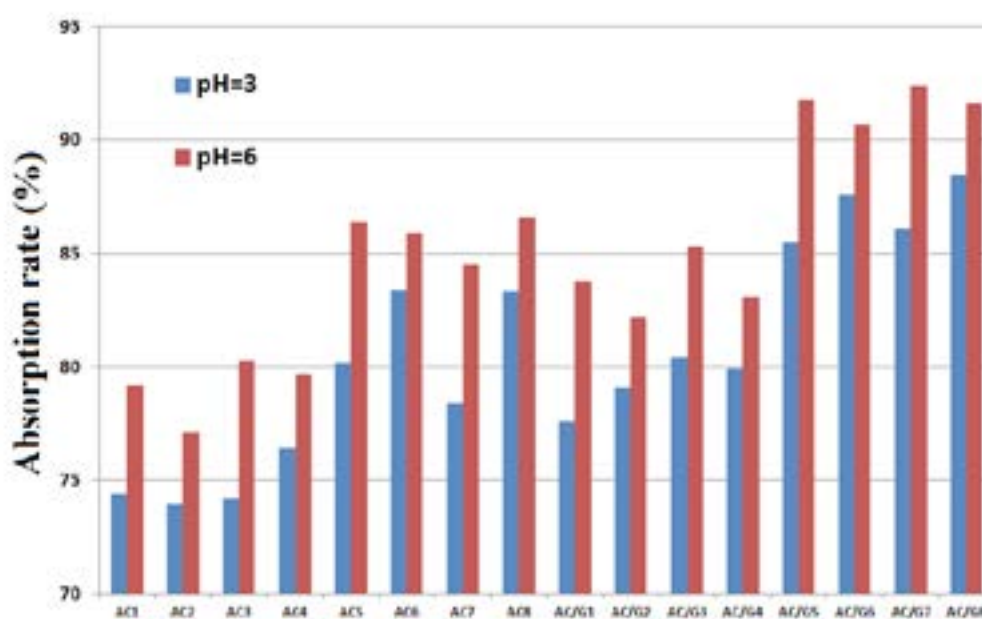


Fig. 5. Comparison of the effect of pH on arsenic removal under various laboratory conditions.

Table 4. The Increasing adsorption of arsenic by the presence of graphene in the adsorbent structure.

amount of adsorbent (mg)	Initial concentration (mg As L ⁻¹)	Time of absorption (min)	pH=3 Increase in absorption (%)	pH=6 Increase in absorption (%)
100	100	60	3.2	4.6
100	200	60	5.1	5.1
200	100	60	5.3	5.4
200	200	60	4.2	4.8

are compared with each other over a period of 60 minutes. According to Table 4, it is observed that in the same condition, the presence of graphene increases the amount of arsenic absorption.

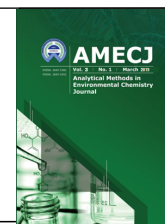
According to Table 4, the presence of graphene in neutral pH (pH = 6) has a greater effect on the absorption rate due to the intrinsic effect of more graphene porosity on the total of the adsorbent. Moreover, the lack of ionic resistance in adsorption of arsenic could also point to the phenomenon of favorable spatial inhibition between graphene sheets in neutral media due to the negative charge found in the graphene agent groups of Hammers. That way, by increasing the pH of the environment, the presence of positive ions in the wastewater decreases, and the tendency to converge graphene plates in the composite weakens. As a result, adsorption of arsenic by composite adsorbent with less resistance and more surfaces by graphene is done. This subject occurs with the same intensity in the 120-minute adsorption period. Due to the presence of graphene in the structure of activated carbon, the effect of absorbing time is insignificant. In addition, due to the structural nature of the adsorbent and the low concentration of arsenic, better adsorption is there in the process. Therefore, it is observed that with the presence of less adsorbent, the greatest effect of pH in the adsorption process is due to the presence of graphene in the adsorbent structure which increases the absorption to about 1.4 times. That is, graphene greatly enhances the effect of the pH of the wastewater, in other words, when the composite absorbent is used, the sensitivity of the adsorption process to higher pH changes should be controlled with greater precision and be limited to higher pH.

4- Conclusion

Activated carbon as one of the most suitable and efficient adsorbents in adsorption of arsenic in industrial effluents has a good performance, so that it can separate about 86.6% of arsenic from wastewater during 120 minutes. Because the adsorption process carried out by activated carbon is related to porosity and ion exchange, it is attempted to upgrade these parameters by changing its structure. For this purpose, the graphene structure of Hammers, which has a very high porosity and anionic surface charge, as a modern idea is used in this research. It has been observed that the presence of graphene in the adsorbent structure has caused a significant increase in the amount of adsorption of arsenic, so that in optimum conditions, the adsorption rate increased up to 91.8%. On the other hand, the absorption time of more than 60 minutes have not had any significant effects on absorption, and this process causes the more economical due to requiring of shorter time for balancing the maximum absorption. Moreover, by observing the effect of wastewater pH, graphene performance has been improved at higher pH values due to the force of dissolved ion potential difference at the rate of adsorption of arsenic by composite absorber. Therefore, it can be controlled by adjusting the pH of wastewater, and the use of corrected graphene structures easily controls the absorption process and increases the efficiency of absorption. Also, it has been observed that with increasing arsenic concentration, the absorbent performance of the composite is weakened. Due to the sensitivity of the presence of arsenic in released wastewater, these types of adsorbents are suitable for final purification and dilute wastewater.

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A new analytical method based on bismuth oxide-fullerene nanoparticles and photocatalytic oxidation technique for toluene removal from workplace air

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ABSTRACT

A new sorbent based on mixture of bismuth oxide-fullerene nanoparticles ($\text{Bi}_2\text{O}_3\text{-NF}$) was used for degradation/removal of toluene from workplace and artificial air by UV-photocatalytic oxidation method (UV-PCOM). By set up of pilot, standard gas of toluene was generated with difference concentrations, and then was passed through UV lamp-glass quartz cell accessory (UV-GQC) by SKC pump at optimized flow rate. Following the UV irradiation, the electrons and holes can undergo redox reactions with toluene on the Bi_2O_3 surface that lead to the formation of toluene intermediates and toluene. Toluene and intermediates was physically and radically absorbed on the 200 mg of NF at room temperature and then, desorbed from it at 185 °C before determined by GC/FID. In optimized conditions, the adsorption capacity and removal efficiency of NF were obtained 212 mg g^{-1} and more than 95%, respectively. The chemically absorption mechanism of toluene on NF was mainly obtained due to radically group of NF ($\text{OH}^\bullet$, $\text{CO}^\bullet$) with methyl of toluene ($\text{CH}_3^\bullet$) and physically adsorption depend on characterization of NF. In addition the flow rate and temperature had highly impact on NF for removal efficiency and absorption capacity of toluene from workplace and artificial air.

Introduction

The most Pollutants such as volatile organic compounds (VOCs, BTEX) and semi-volatile compounds (SVOCs, Di-nitrotoluene) release to air and environment by various industrial processes and human activity such as petrochemical facilities, motor vehicles, metal processing/finishing industries, gas stations, and energy sectors. Transport-derived emissions of volatile organic compounds (VOCs) have decreased owing to

stricter controls on air pollution. The high fraction of volatile chemical products (VCP) emissions is consistent with observed urban outdoor and indoor air. VCP contribute fully one-half of emitted VOCs in industrialized cities. Based on previous study, the toluene concentration was the most predominant among all the targeted compounds in air. So, removal of toluene from air is very important [1-5]. These compounds (VOCs) are associated with allergies and adverse respiratory effects [6] and some of them have been classified as carcinogenic to humans (benzene, formaldehyde) by the International Agency for Research on cancer [7]. A complex

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combination of physicochemical and biological phenomena takes place to finally convert pollutants into innocuous compounds (mostly CO_2 , H_2O and biomass)[8]. The accumulation of VOCs is the greatest problem in air atmospheric pollutions with cars or industrial activity. The BTEX pollutants (benzene, toluene, ethylbenzene and xylenes) generated in air by gasoline combustion in car engines and caused a risk to human health[9]. The BTEX have a carcinogens effect in humans. They readily volatilized and distributed over large regions of air and have important role in photochemical oxidants and organic aerosols[10]. Among various types of VOCs, toluene is one of the most commonly used substances in industry and commerce as a solvent in paints, silicone sealants, many chemical reactants, rubber, printing ink, adhesives (glues), lacquers, leather tanners, and disinfectants[11, 12]. Most of VOCs are regarded as toxic compounds for human beings and the environment. symptoms associated with exposure to VOCs include eye irritation, nose and throat discomfort, headache, allergic skin reaction, nausea, fatigue, or dizziness, nervous system effects, liver toxicity, cancer[13, 14]. If inhaled or contacted, toluene can cause dermatitis (dry, red, cracked skin) and damage the nervous system and kidneys[12, 15]. The 8-h time-weighted average (TWA) for occupational exposure to toluene in accordance with ACGIH, OSHA, NIOSH methods is respectively 50, 200 and 100 ppm. Therefore, toluene emission control has become more stringent. Growing concerns on exposure to toxic air pollutants has led to intensive search for the best available technology for remediation of air pollutants[16, 17]. A number of physical, chemical and biological technologies such as membrane separation[14], adsorption[18], catalytic oxidation[19] and advanced oxidation[20] have been developed to remove VOCs successfully. The control of toluene emission is often accomplished by catalytic oxidation or adsorption. The adsorption process is widely used as a simple and effective operation[21]. Adsorption of VOCs by activated carbon (AC) has proven to be sustainable, environmentally

friendly, economical and efficient which makes it the most commonly used technique[22]. Toluene removal by adsorption is the traditional method for cleaning air contaminants [23-25]. However, the use of adsorbents just transfers pollutants from the gaseous phase to the solid phase and causes a disposal and regeneration problem[15]. Many studies have been done to remove toluene using carbon adsorbent such as activated carbon fibers (ACFs)[22], NaOCl oxidized carbon nanotubes[26], Zeolite[15], Nanographene modified by ionic liquid[27]. Buckminsterfullerene (C_{60}) a hydrophobic molecule comprise a class of nanomaterials that are made of a newly discovered allotrope of carbon and composed of 60 carbon atoms arranged in a hollow spheres, ellipsoids, or tubes spherical shape, has gained wide application in many industries, including biomedical technology, electronics, optics, and cosmetics[28-30]. In recent years, advanced oxidation processes have been considered as a way to pollute organic pollutants. These methods are based on the production of highly active species such as hydroxyl radicals ($\text{OH}^\bullet$) that can oxidize a wide range of organic pollutants. Among the advanced oxidation processes, heterogeneous photocatalytic are used as a successful method for the analysis of organic pollutants[31-33]. Degradation of volatile organic compounds such as, o-xylene, n-hexane, n-octane, n-decane, methylcyclohexane and 2,2,4-trimethylpentane in the gas phase by heterogeneous photocatalysis with titanium dioxide/ultraviolet light was achieved at 52-62°C. in this way, devices based on heterogeneous photocatalysis do not need flame for VOC oxidation, this will allow it to be installed safely even in areas vulnerable to fire and explosion[34, 35]. In this study, the UV-PCOM based on Bi_2O_3 -NF was used for efficient removal of toluene from air. The Bi_2O_3 /UV irradiation increased the removal efficiency of toluene from air by chemically adsorption of NF. Experimental parameters such as concentration, UV irradiation, temperature, the value of Bi_2O_3 -NF, flow rate, contact time, desorption, absorption, and repeatability were studied and optimized.

The performance of the proposed method was evaluated.

2. Experimental

2.1. Instrumental:

Gas chromatography (GC) was used for determination of toluene in air (Agilent, Netherlands). The FID detector was selected for toluene analysis in air/gas. The polyethylene tubes (PET) are simple devices that introduce a pure air stream from *electro air cleaner (EAC, Canada, model HEPA 600M)* into bags. Adjusted valves are used to control of gas flow rate from Germany. For sampling, the air bags, septum port and air sampling apparatus were used. GC equipped with a split/splitless injector, FID, and a column coated with cross-linked polydimethylsiloxane gum (50 m $\times$ 0.2 mm id.). For determining of toluene with GC, The temperature of injector and detector was adjusted to 200°C and 270°C, respectively. The temperature of oven was tuned from 50°C to 140°C which was held for 10 min. Hydrogen as the carrier gas was used at a flow rate of 1.0 mL min⁻¹ with split ratio of 1:100. The different volumes of glass vials (10-200 mL, Aldrich, Germany) with air tight cap (PTFE) were used in batch or static system. The polyethylene tubes and bags were used as a transport and storage of air in static/dynamic system. TGS 2180 (China) and Dräger Pac 3500 (Lübeck, Germany) detectors were used for continuous measurement of H₂O vapor and O₂ concentrations in gas fluid, respectively. The TGS detector has high sensitivity to water vapor and its conductivity depends on absolute humidity (0.7~150 gm⁻³). Preheat of tubes and bags caused to capture water droplets. The toluene evaporated from chamber accessory, mixed with purified air and introduced to bags. For validation of methodology, the concentration of toluene in polyethylene bags was determined by GC-MS before and after passed through Bi₂O₃-NF. The quartz glass tube (QGT, 10 cm) as a column sorbent was used for Bi₂O₃-NF. In this study, QGT with 0.4 cm diameter and 10 cm length was filled with 200 mg of Bi₂O₃-NF. The gas tight syringes (SGE) were used for

sampling of toluene and injection to GC. In this study, toluene generation system, QGT, PET, bags, electric power supply accessory (50-280 V_{AC}, 10A, 20-800 °C, Italy), pneumatic valves (Germany) and Ar gas were used for evaluation of toluene removal from air. The accuracy of results was achieved by injecting a standard concentration of toluene in the chamber accessory before determined by GC-FID/GC-MS.

2.2. Reagents and solutions

All reagents with high purity and analytical grade were purchased from Merck and sigma Aldrich (Darmstadt, Germany). All aqueous solutions were prepared in ultra-pure deionized water ($R \geq 18 \text{ M}\Omega \text{ cm}^{-1}$) from Milli-Q plus water purification system (Millipore, Bedford, MA, USA). The analytical grade of toluene solution was purchased from Sigma Aldrich, Germany (CAS N: 108-88-3, 99.8%). For calibration of toluene, the approximate concentrations of toluene in methanol were prepared by 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 2.0, and 5.0% (v/v). The analytical grades of other reagents such as, HNO₃, HCl, methanol, ethanol and acetone were prepared from Merck (Germany). Bismuth nitrate (Bi(NO₃)₃·5H₂O), sorbitol and distilled water used for the preparation of Bi₂O₃ nanoparticles. Bismuth nitrate (CAS N: 383074) and sorbitol (CAS N: 50-70-4) were purchased from Sigma Aldrich. The solutions were freshly prepared and stored just in a fridge (4 °C) to prevent decomposition. All the laboratory glassware and plastics were cleaned by soaking in nitric acid (10%, v/v) for at least 24 h and then rinsed with deionized water before use.

2.3. Synthesis bismuth oxide and fullerene nanoparticles

Bismuth oxide nanoparticles (BONPs) were prepared by special solid dispersion evaporation technique (SDAT) with carrier solutions such as sorbitol and flame sprays pyrolysis technique (FSP) by organodimethicone (ODIM). By SDAT Synthesis, 5 g of solid bismuth nitrate [Bi(NO₃)₃·5H₂O] dissolve in carrier solutions (5 ml) and stirred for 20 min at room temperature followed

by sonication at 25 °C in an ultrasonic bath (40 kHz and 100 W). The mixture was diluted with 10 mL of distilled water and put on heater magnet stirrer plate for 30 min. The pH of sample solution was optimized up to 7 and no precipitation was occurred during processes. The oven provided programmable heating up to 90–110 °C for 50 min. Then dark brown sediment was formed after the evaporation of water. After 1 hour yellow sediment was formed in 550–600 °C and nano particles is decomposed at 800–1200 °C. In order to obtain pure BONPs and remove the metal nanocatalysts, the product was stirred in 18% HCl solution for about 16 h at an ambient temperature. Then, the sample was washed repeatedly (10N) with deionized water until the solution became neutral. The treated product was finally dried in oven at 100 °C. So, bismuth nitrate, sorbitol and distilled water used for the preparation of Bi_2O_3 nanoparticles medical grade by proposed procedure. For synthesis of fullerene (NF), fullerene soot (FS) was purchased from Sigma-Aldrich and pure fullerene (NF) was achieved with activated carbon and silica gel (TEM size: 30–100 nm) [36]. The pure fullerene (C60) from fullerene soot (FS) was done by two methods. By first procedure, a Soxhlet extractor with toluene was used for separation of light and heavy fullerenes (Fig. 1). The electric arc was used for producing of FS with low purity up to 7%. The second way was obtained

by column chromatography with stationary phase and mobile phase of activated carbon/ silica gel and chlorobenzene, respectively.

2.4. Characterization

The morphology of the mesh sorbent Bi_2O_3 and NF was examined using scanning electron microscopy (SEM, Phillips, PW3710, Netherland) and transmission electron microscopy (TEM, CM30, Philips, Netherland). The nanoparticle powder of Bi_2O_3 is dissolved in water or ethanol with ultrasonic bath and after drying, was prepared for TEM in scale of 50–100 nm. The elemental composition of the samples was tested by energy dispersive X-ray microanalyser (EDX, QuanTax 200, Rontec, Germany) which was attached to SEM. X-ray diffraction (XRD) patterns for Bi_2O_3 nanoparticles were recorded by a GBC MMA diffractometer with beryllium-filtered Cu K α radiation (1.55 Å) operating at 35.3 kV and 30 mA. FT-IR 8400 (Kyoto, Japan); UV-vis spectrophotometers Scinco S-2100 (SCINCO, Twin Lakes, WI, USA), NMR Jeol 90 MHz (JEOL Ltd., Tokyo, Japan), and rotary evaporator (Heidolph Laborota 4000, Schwabach, Germany) were used for nanofullerene (NF) characterization.

2.5. Removal Procedure

The concentration of toluene vapor in pure air was

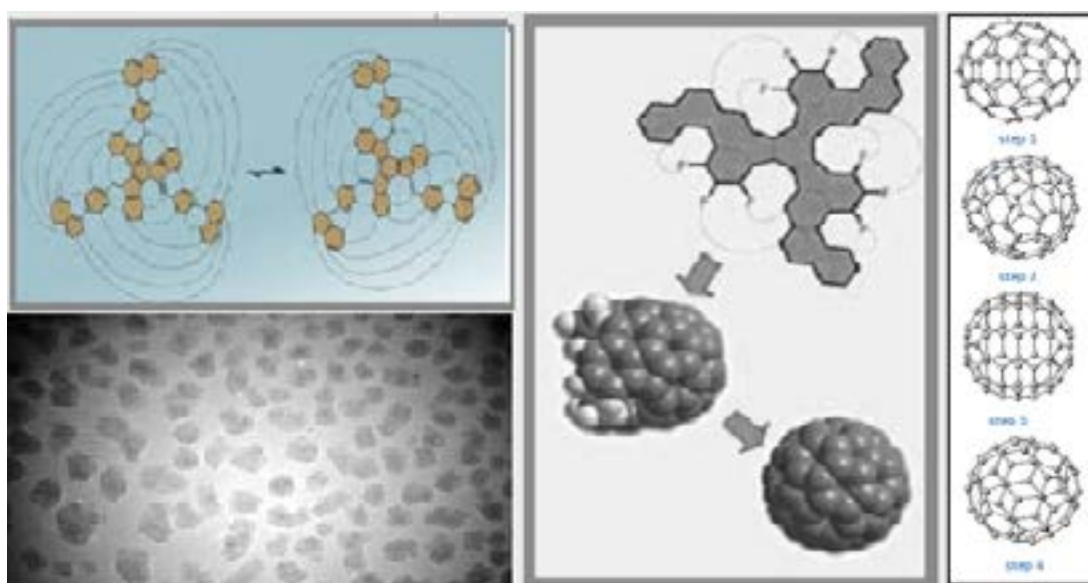


Fig. 1. The schema of light and heavy fullerenes

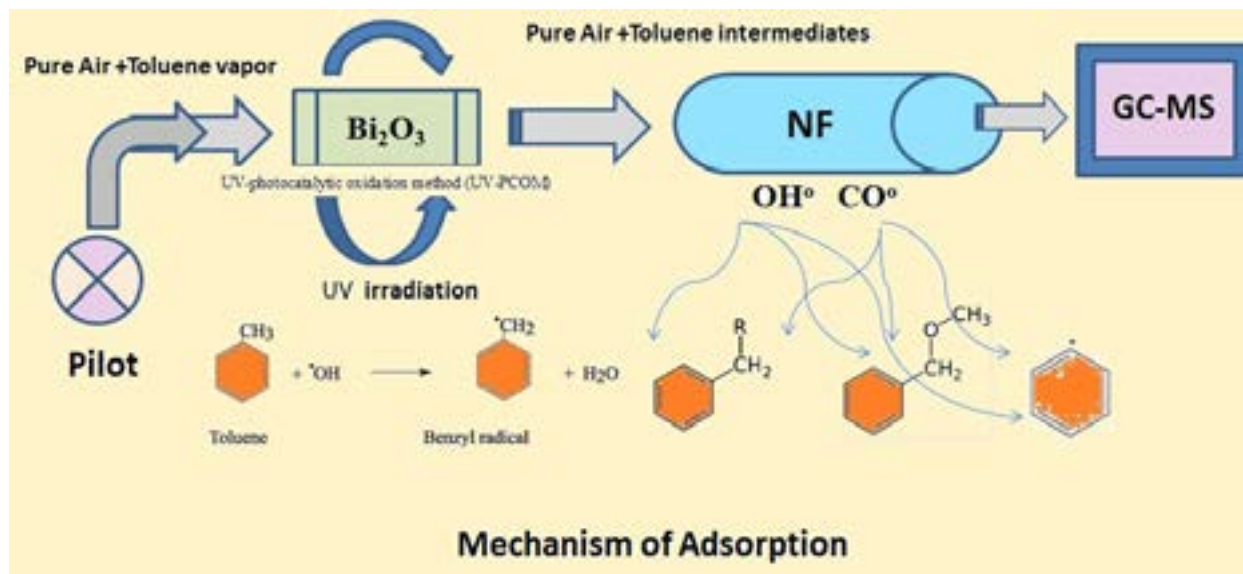


Fig. 2. The pilot of toluene vapor generator in pure air and adsorption procedure

prepared by pilot chamber (Fig. 2). The toluene vapor was generated by and mixed with pure air (210 mL of O_2 per L; 2.5 mL of H_2O per L) at $25^\circ C$. This mixture was restored in polyethylene bag (5 Lit) and toluene was determined by GC-MS and GC-FID. Based on producer, in bath scale set up, 10 mL of standard solutions of toluene (40-100 mg) was convert to vapor gas and mixed to pure air and then pass through silica gel and Bi_2O_3 nanoparticles with flow rate of 500 mL min^{-1} at 10 min which was irradiated by UV in quartz glass tube (QGT). Then, toluene and intermediates was absorbed on NF by physically and radically formation. Finally, toluene and intermediates desorbed from NF at $185^\circ C$ before determined by GC/FID. For validation of methodology, GC-MS and spike of sample was used. This method can be applied for toluene removal from artificial and workplace air.

3. Results

In this research, Bi_2O_3 -NF was used for efficient removal of toluene from air. The Bi_2O_3 based on UV irradiation can be increased the removal efficiency of toluene from air by radically adsorption. The characterization of Bi_2O_3 /NF such as TEM, SEM, XRD, XRD and IR was prepared. The important parameters include, toluene concentration, intensity of UV irradiation, temperature, the mass of Bi_2O_3 -NF, flow rate, time and repeatability were studied

and optimized.

3.1. TEM, SEM, XRD and IR

The results of synthesis for Bismuth oxide nano particles have been obtained in a series of scanning electron microscope (SEM) and transmission electron microscopy (TEM) images. It was clarified that the size of nanoparticles are obtained below 100 nm. The TEM and SEM images of Bi_2O_3 have been demonstrated in figure 3 (a, b). SEM and TEM of fullerene nanoparticles (NF) was shown in figure 4(a, b) which was between 50-100 nm. The XRD of Bi_2O_3 and NF was shown in figure 5 a and 5b, respectively. The IR of NF (C60) was shown in figure 6.

3.2. The effects of humidity

The concentration of toluene vapor in pure air was prepared at $25^\circ C$ (210 mL of O_2 per L; 2.5 mL of H_2O per L). This mixture was restored in 5 Li of polyethylene bag. Finally, toluene vapor in pure air was removed from air by UV-PCOM method. By procedure, the effects of humidity on adsorption capacity of Bi_2O_3 -NF in QGT were examined in different humidity (10-60%). The value of humidity in the pilot chamber was adjusted by the water tank valve by auto electronic system in present of silica gel. By increasing of humidity more than 40%, the removal efficiency of Bi_2O_3 -NF was

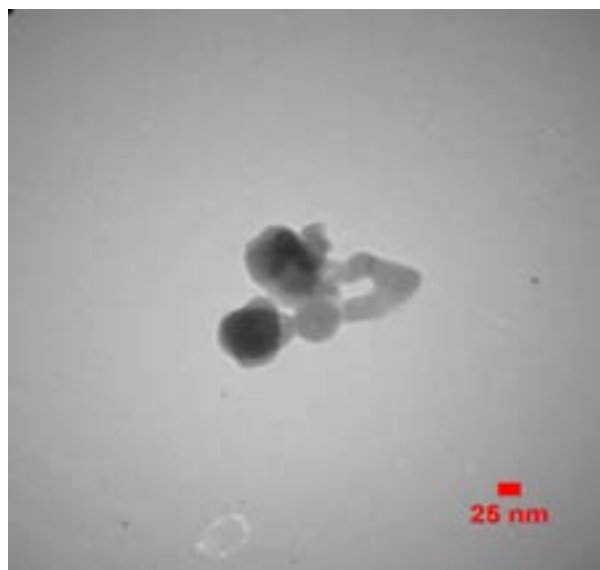


Fig. 3a. TEM picture of Bi_2O_3

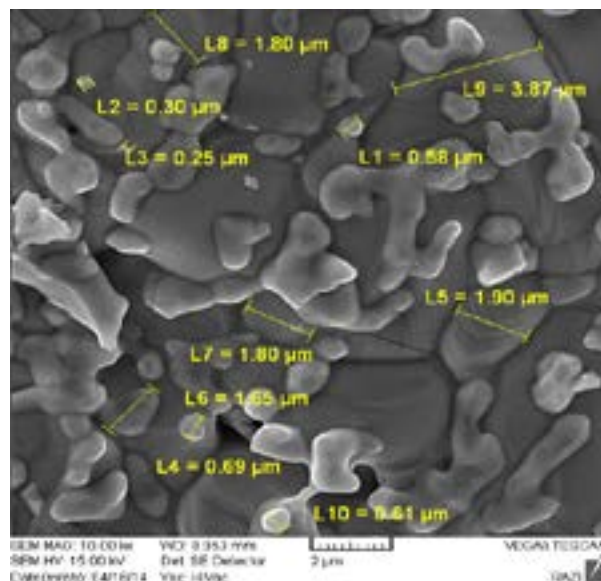


Fig. 3b. SEM picture of Bi_2O_3

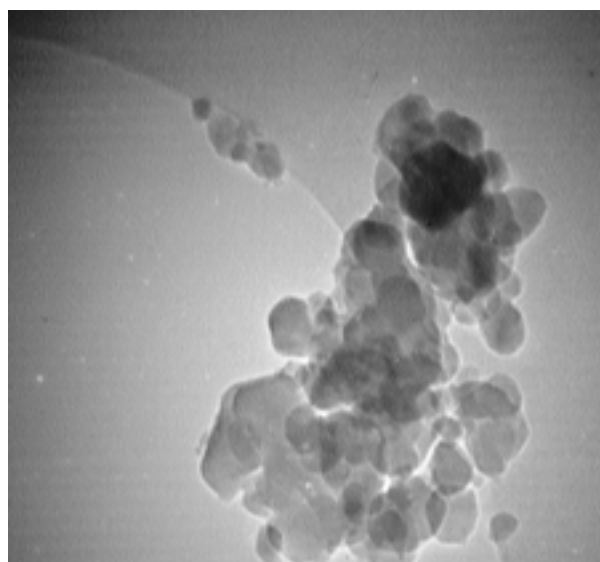


Fig. 4a. TEM picture of NF

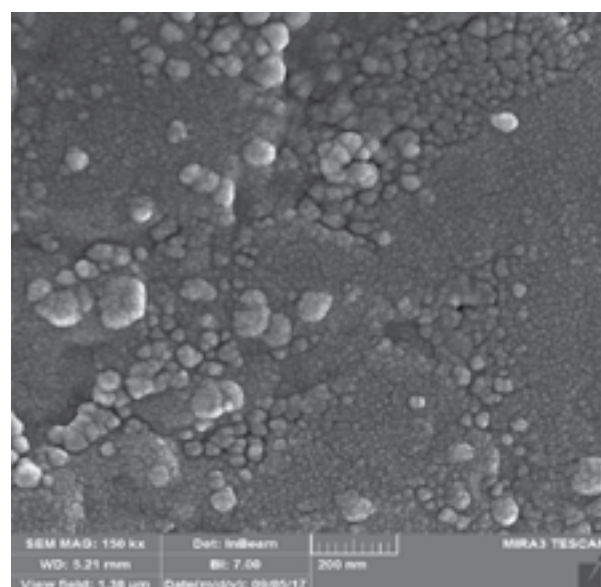


Fig. 4b. SEM picture NF

decreased (Fig. 7). The Previous study showed that the trap device packed with silica composite – multi walled carbon nanotubes (MSN-MWCNTs) prepared based on sol–gel technique was used for evaluation of volatile organic compounds at 20% humidity. Increasing of humidity may be reduced the adsorption active sites on NF which was occupied by water ($-\text{OH}$). On the other hand, the nanoparticles of NF stick together with water molecules increase in size and decrease of surface

area. All examinations were achieved by toluene concentration (40 mg L^{-1}), flow rate (500 mL min^{-1}), temperature (25°C), and 200 mg of Bi_2O_3 -NF. In optimized condition, the 20% humidity had low effects on toluene removal from air less than 5%. Also, the results showed us, the humidity had lower effect than temperature.

3.3. The effect of toluene concentration

By optimizing conditions, the toluene removal

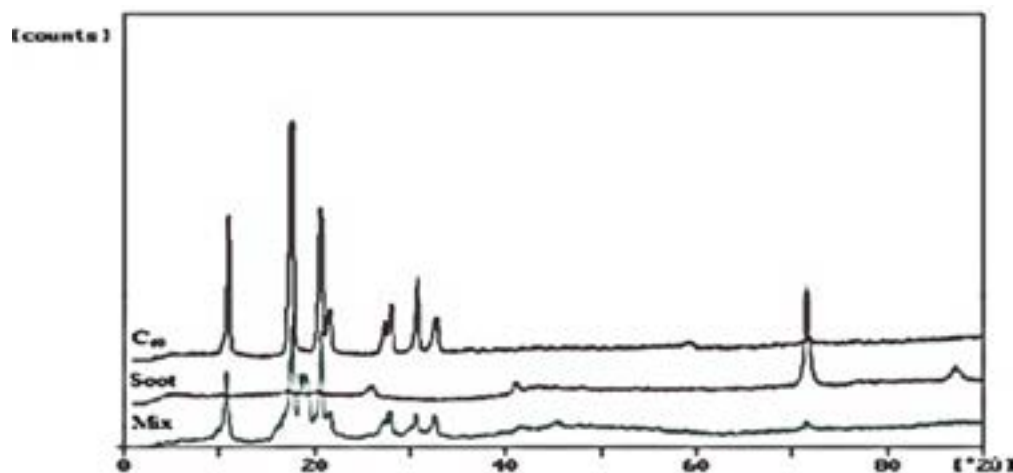


Fig. 5a. XRD spectra of NF

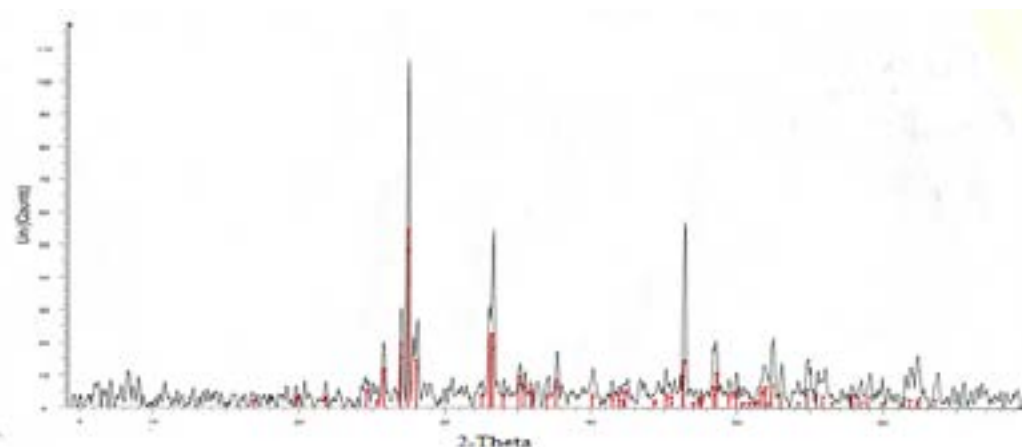


Fig. 5b. XRD spectra of Bi_2O_3

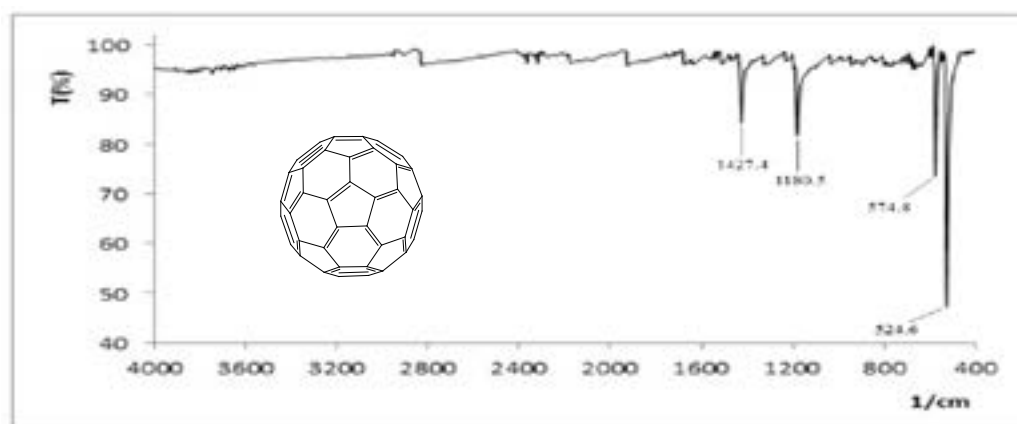


Fig. 6. The IR spectra of NF

from air based on Bi_2O_3 -NF was studied in different toluene concentration from 10-100 ppm (mg L^{-1}). The high surface area in NF based on UV lamp-glass quartz cell accessory (UV-GQC) caused to increasing of the adsorption capacity for toluene

removal from air. At high concentration of toluene, the Bi_2O_3 -NF can be acted as a favorite sorbent. The optimum of toluene concentration for removal efficiency (>99%) with 200 mg of Bi_2O_3 -NF, NF, Bi_2O_3 was achieved, 42.4 mg L^{-1} , 20.6 mg L^{-1}

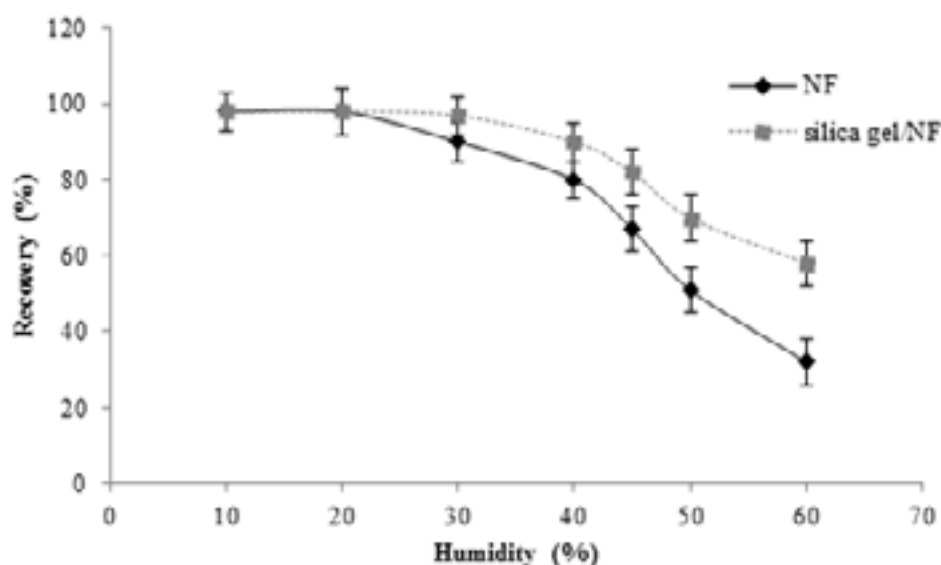


Fig.7. The effects of humidity on toluene adsorption by silica gel/ Bi_2O_3 -NF

and 2.3 mg L^{-1} in 25°C , respectively. The results showed, in optimized concentration, the Bi_2O_3 -NF had more adsorption capacity and removal efficiency than others.

3.4. The effect of temperature

The temperature has a main factor for removal efficiency of toluene from air by Bi_2O_3 -NF. As prevent to condensing toluene, the special thermal accessory was used in pilot chamber for heat controlling up to 115°C . The column of QGT was used at below 45°C . The effect of temperature was studied between 20 – 200°C . The results showed us, the absorption recovery of Bi_2O_3 -NF was depended to temperature. Desorption of toluene from Bi_2O_3 -NF was occurred at 185°C . In optimized conditions, the removal recovery for toluene based on Bi_2O_3 -NF was more than NF up to 45°C (Fig. 8). Sone et al showed that the adsorption of toluene was decreased by increasing temperature. Increasing temperature more than 50°C had negative effects on removal efficiency of Bi_2O_3 -NF and had more effected on humidity. In this study, the adsorption capacity of Bi_2O_3 -NF and NF has obtained 212 mg g^{-1} and 99.6 mg g^{-1} , respectively. Other parameters such as, the surface area, flow rate, kind/ porosity/ source/ size sorbent and chemical and physical adsorption can be affected on removal of toluene from air. The low adsorption capacity of nanosorbents related to

greater amounts of amorphous structure with low surface area or increasing of temperature.

3.5. The effect of sorbent mass

The amounts of Bi_2O_3 -NF (1:1) as a sorbent in the range of 20 to 300 mg were tested on the recoveries of toluene removal from air at 25°C . It was found that 220 mg of Bi_2O_3 -NF was sufficient for quantitative recoveries of toluene removal from air. Extra mass of Bi_2O_3 -NF had no significant effect on the efficient removal of toluene vapor in air. So, 200 mg of Bi_2O_3 -NF was selected as an optimized mass sorbent by UV-PCOM. Also, the Bi_2O_3 and NF and Bi_2O_3 -NF had maximum recovery up to 5.1% and 48.4% and more than 95%, respectively. These results confirm that the radically group of NF (OH° , CO°) with methyl of toluene (CH_2°) had important role for removal of toluene in present of Bi_2O_3 by UV-PCOM.

3.6. The effect of flow rate

The flow rates were optimized in order to obtain the maximum recovery by proposed method. So, the effect of different flow rates between 100 to 1000 mL min^{-1} was examined by Bi_2O_3 -NF at room temperature. The flow rate was measured by a digital rotameter in input and output of QGT in optimized conditions. The results showed us, the removal efficiency and adsorption capacity of Bi_2O_3 -NF

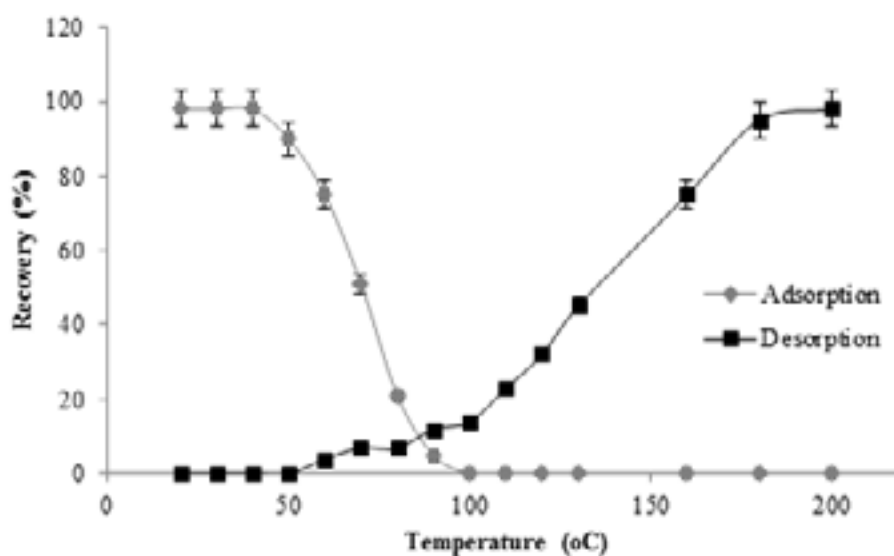


Fig. 8. The effects of temperature on toluene adsorption and desorption from Bi₂O₃-NF

was decreased in more than 550 mL min⁻¹ of flow rate. So, 500 mL min⁻¹ of flow rate was selected as optimum flow rate for removal of toluene in air. Higher flow rate was significantly decreased the adsorption recovery of Bi₂O₃-NF. Based on results, the maximum of toluene adsorption by exterior and interior sites of NF was obtained at less than 500 mL min⁻¹. Figure 9 show the effects of difference flow rate on the removal efficiency and adsorption capacity in optimized conditions.

3.7. Method Validation

Due to obtained Results, the Bi₂O₃-NF was selected as a novel sorbent for removal of toluene vapor from air. By proposed method, a mixture of 10–100 ppm of toluene vapor which was generated by pilot, storage in PE bag (5 L). Then, the mixture of toluene in artificial air moved to Bi₂O₃-NF in present of argon gas as a carrier gas. The different standard of toluene (mg) in air was validated by high sensitive and accurate GC-FID/GC-MS before using by UV-PCOM. Since no certified reference

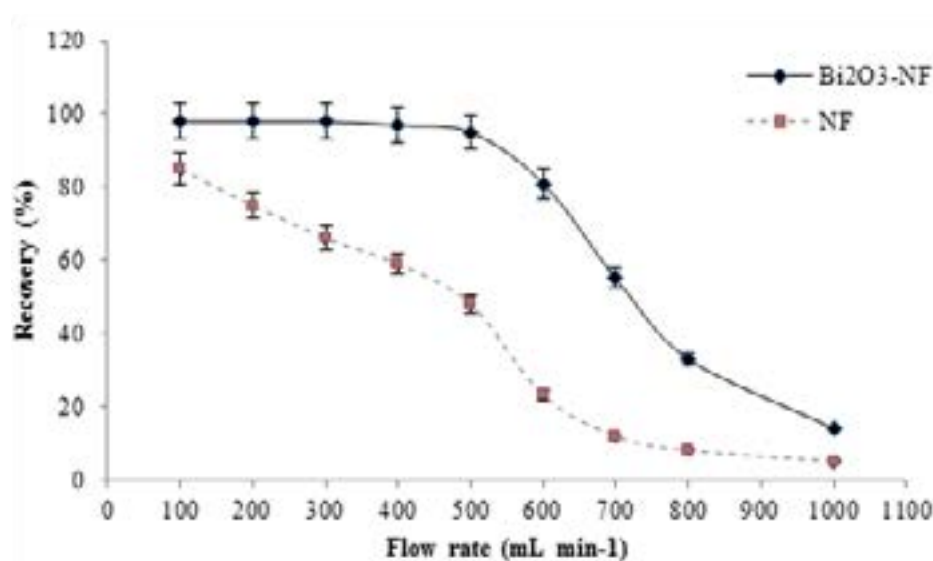


Fig. 9. The effects of flow rate on toluene removal by Bi₂O₃-NF and NF

Table 1. Method validation based on by spike of toluene concentration in artificial air by Bi₂O₃-NF/GC-FID (mg L⁻¹)

Tolene ^a	Bag of pilot	Spike of toluene	Results ^b	Recovery (%)
1.0	0.93 ± 0.04	1.0	1.79 ± 0.05	96.2
5.0	4.58 ± 0.27	5.0	8.89 ± 0.46	97.1
10.0	9.43 ± 0.53	5.0	14.19 ± 0.65	101.2
15.0	14.39 ± 0.75	10.0	22.54 ± 1.23	94.6
20.0	19.70 ± 0.96	10.0	28.57 ± 1.33	98.2
25.0	24.65 ± 1.14	15.0	40.11 ± 2.16	102.7

^a (Flow rate 500 mL min⁻¹, Peak Area of GC-FID, 200 mg, T=45°C)^b (Mean of three determinations ± confidence interval, P = 0.95; n = 5)

material (CRM) for toluene in air are currently available, the spiked of toluene concentration (10-100 ppm) were used for validation of proposed method. At optimized conditions in 5 and 10 minute, 20 ppm and 40 ppm of toluene vapor in air was almost removed by Bi₂O₃-NF, respectively (bag 5 L). The efficient recovery of spiked samples is satisfactorily reasonable which indicates the power ability of UV-PCOM based on Bi₂O₃-NF for removal of air toluene. After thermal desorption of Bi₂O₃-NF in QGT, the toluene concentration was on-line determined by GC-FID. The validation of methodology was confirmed using GC-MS (Table 1, 2).

4. Discussion

Volatile organic compounds (VOCs) are released from various sources such as chemical processing industries involved with the manufacturing, handling, and the distribution of paints, lubricants, and liquid fuels and are unsafe for human health are

known to have and environmental functions[37]. The numerous VOC treatment technologies have emerged, such as incineration, condensation, biological degradation, absorption, adsorption, and catalysis oxidation. One of the common techniques to monitor BTX in ambient air is the use of a sorbent/solvent for the trapping and extracting of VOCs from air or gas[38]. In this study, the toluene removal from air was investigated based on mixture of bismuth oxide-fullerene nanoparticles (Bi₂O₃-NF) by UV-photocatalytic oxidation method (UV-PCOM). The obtained results showed that flow rate and temperature had highly impact on NF for removal efficiency and absorption capacity of toluene from air. Many researchers investigated on toluene removal from air based on various absorbents. The removal of toluene from air through Nano-graphene modified by ionic liquid (NG-IL) was studied. In this study the effect of different conditions such as; toluene concentration, humidity, and temperature on the adsorption were investigated. The results showed the adsorption

Table 2. Comparing of Bi₂O₃-NF, Bi₂O₃ and NF for removal of toluene from artificial air by GC-FID/GC-MS (mg L⁻¹)

Sorbent*	Bag	Added	GC-FID ^a	GC-MS ^a	GC-FID Recovery (%)	GC-MS Recovery (%)
NF	5.0	-----	2.34 ± 0.02	2.45 ± 0.02	46.8	49.0
		5.0	4.53 ± 0.03	4.78 ± 0.04	43.8	46.6
		10.0	6.68 ± 0.04	7.09 ± 0.05	43.4	46.4
Bi ₂ O ₃ -NF	5.0	-----	4.88 ± 0.05	4.93 ± 0.06	97.6	98.6
		5.0	9.71 ± 0.09	9.77 ± 0.10	96.6	96.7
		10.0	14.95 ± 0.15	14.64 ± 0.16	101.1	97.1
Bi ₂ O ₃	5.0	-----	0.74 ± 0.03	0.77 ± 0.04	1.5	1.5
		5.0	1.43 ± 0.07	1.51 ± 0.05	1.4	1.5
		10.0	2.24 ± 0.12	2.33 ± 0.09	1.5	1.6

^a (Mean of three determinations ± confidence interval, P = 0.95; n = 5)* (500 mL min⁻¹ air flow rate, 200 mg, T=45°C)

capacity was decreased by raising the sorbent humidity above 50 percent and the toluene capture capacity for NG-IL was 126 mg g^{-1} which was lower than $\text{Bi}_2\text{O}_3\text{-NF}$ [27]. By UV-photocatalytic oxidation method, the capacity of toluene absorption with $\text{Bi}_2\text{O}_3\text{-NF}$ was 212 mg g^{-1} which was depended to UV-photocatalytic oxidation. Lillo-Ródenas showed that the removal percentage for toluene also may depend on porosity and the surface chemistry of adsorbent. They showed that adsorption capacities for benzene and toluene was obtained 34 g per 100 g activated carbon(AC) and 64 g per 100 g, respectively which is lower than $\text{Bi}_2\text{O}_3\text{-NF}$ by UV-PCOM [39]. Surface chemistry of activated carbon has an important role on the removal of aromatic compounds in air because it affects both electrostatic and dispersive interactions between adsorbents and adsorbates [40]. In proposed method, the chemically absorption of toluene on NF mainly obtain due to radically group of NF (OHo, COo) with methyl of toluene (CH_2o). Rezaei et al. have been used as complex system of nano-particles of titanium dioxide on exposing them by ultraviolet radiation. The results showed titanium dioxide nanoparticles when subjected to ultraviolet radiation ,exhibit strong oxidizing and regenerative properties and can be used to remove toluene vapors in high concentrations but it need more time for adsorption process and titanium dioxide nanoparticles is expensive as compare to carbon compounds [41]. In addition, the use of a suitable adsorbent according to the type of sorption can be helped for removal toluene from air. Ichiura at el. has suggested a sorbent based on zeolite or activated carbon as a photocatalyst bed to improve the efficiency of adsorption with higher recovery [42].

Shojaee showed that ZSM-5 has a porous surface with surface area of 356.4 m^2 per gram. That after the calcination at temperature of 450°C it decreased to 332.5 m^2 per gram. The results of the photocatalytic degradation process showed that the best performance of ZSM-5/ TiO_2 bed was at concentration of 50 ppm , so that was able to remove 75% toluene vapors which was lower than

$\text{Bi}_2\text{O}_3\text{-NF}$ [43,44]. According to obtained results, removal of toluene from air based on $\text{Bi}_2\text{O}_3\text{-NF}$ / UV-PCOM was very rapid and absorption capacity increased up to 212 mg per gram. Rezaee et al. studied on the potential of MnO/GAC and MgO/GAC composites for toluene adsorption from air stream. They showed that, by increasing inlet toluene concentration from 100 to 400 ppm, the breakthrough time of MgO/GAC and MnO/GAC was decreased [45]. So, the proposed method based on $\text{Bi}_2\text{O}_3\text{-NF}$ had many advantages such as, high efficiency, simple, low cost for toluene removal from air as compared to other methods.

5. Conclusions

In this study, the removal of toluene from air was obtained based on $\text{Bi}_2\text{O}_3\text{-NF}$ and UV-PCOM. By procedure, many advantages such as, high efficiency, high capacity, low cost, simple and fast adsorption was achieved. In optimized conditions, toluene concentration, $\text{Bi}_2\text{O}_3\text{-NF}$ mass, temperature and flow rate were evaluated. The capacity of sorbents, recovery, and removal efficiency of $\text{Bi}_2\text{O}_3\text{-NF}$, Bi_2O_3 and NF was studied by CG-FID and GC-MS. Based on the results, the recovery of $\text{Bi}_2\text{O}_3\text{-NF}$ was more than Bi_2O_3 and NF sorbents. Also, the maximum adsorption of toluene was achieved with 200 mg of $\text{Bi}_2\text{O}_3\text{-NF}$ by flow rate of 500 mL min^{-1} (45°C). Thermal accessory was used for toluene desorption from $\text{Bi}_2\text{O}_3\text{-NF}$ at 180°C . Due to characteristics of $\text{Bi}_2\text{O}_3\text{-NF}$ based on physically and radically adsorption, toluene was efficient removed from air by proposed method.

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