

# Separation of aniline from water and wastewater samples based on activated carbon nanoparticles and dispersive solid phase extraction procedure

Saeed Fakhraie<sup>a,\*</sup>, Morteza Mehdipour Rabouri<sup>b</sup> and Ahmad Salarifar<sup>c</sup>

<sup>a</sup> Chemistry Department, Yasouj University, P.O. Box 74831-75918, Yasouj, Iran.

<sup>b</sup> Occupational Health Engineering Department, Kerman University of Medical Sciences, Kerman, Iran

<sup>c</sup> Environmental Engineering, Faculty of Natural Resources, Islamic Azad University, Bandar Abbas Branch, Iran

## ARTICLE INFO:

Received 10 Aug 2020

Revised form 4 Oct 2020

Accepted 22 Nov 2020

Available online 29 Dec 2020

## Keywords:

Aniline,  
Activated carbon nanoparticles,  
Ionic liquid,  
Dispersive solid phase extraction  
procedure,  
gas chromatography–mass  
spectrometry

## ABSTRACT

The water, wastewater and air are the main sources of aniline in environment. Aniline has a toxic effect in the human body and environment and so, must be determined by novel techniques. In this study, the activated carbon with microwave heating methods (MHM-ACNPs) were used for extraction aniline from waters by dispersive ionic liquid solid phase extraction procedure (D-IL-SPE) and compared to the activated carbon (AC). For this purpose, the mixture of acetone, ionic liquid and 30 mg of MHM-ACNPs/AC added to 100 mL of water samples at pH=8. After sonication for 10 min, the benzene ring in aniline as electron acceptor was chemically adsorbed on carboxylic groups of MHM-ACNPs as electron donors (MHM-ACNPs-COO<sup>-</sup>.....C<sub>6</sub>H<sub>5</sub>-NH<sub>2</sub>) and then, the adsorbent was collected by hydrophobic ionic liquid phase in bottom of conical centrifuging tube. Finally, the aniline was released from MHM-ACNPs in remained solution by changing pH and the concentration of aniline determined by gas chromatography–flame ionization detector (GC-FID). The working range (WR) was obtained from 2.0 to 4000 µg L<sup>-1</sup> (RSD % < 1.8). The detection limit (LOD) and preconcentration factor (PF) and linear range (LR) were achieve 0.6 µg L<sup>-1</sup>, 196.4 and 2.0–950 µg L<sup>-1</sup>, respectively. The proposed method was validated by spiking of real samples and analysis with gas chromatography mass detector (GC-MS).

## 1. Introduction

Aromatic amines such as aniline compounds are employed as the chemical in industries (polyurethane foams) and pharmaceutical product. The reduction of nitrobenzene to aromatic amine can be occurred without adding of metal (zinc, tin, or iron) or dihydrogen in polar solvents. Aniline is an aromatic hydrocarbon and discharge into the

environment through certain industrial effluents which thereby cause to water contamination [1, 2]. Aniline (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>) with benzene ring and NH<sub>2</sub> bond can be reacted to other chemicals with sulfur and carboxyl groups and removed from waters [3]. The main product of aniline is methylene diphenyl diisocyanate (MDI) which was used in polyurethanes as foams in refrigerator insulation. Aniline use in different industries such as paint, polymers, pesticides, herbicides, resins, chemicals, antioxidants, pharmaceuticals, rubber, plastics,

\*Corresponding Author: Saeed Fakhraie

Email: [saeedfakhraie@yahoo.com](mailto:saeedfakhraie@yahoo.com)

<https://doi.org/10.24200/amecj.v3.i04.126>

explosives and solvents in perfumes [4]. It should also be noted that the WHO reported the threshold for nitrobenzene in water is 30–110  $\mu\text{g L}^{-1}$ . EPA showed, water containing aniline at an average of 6–60  $\mu\text{g L}^{-1}$  is not greater than a one-in-a hundred thousand increased chance of developing cancer. Aniline is toxic in humans and cause to mutagenic or carcinogenic effect in the cells of body and DNA [5]. Aniline cause to myelotoxicity, toxicity of lymphoid organs and hematopoietic tissues in human and faunae [6]. Aniline compounds belong to the blacklist of contaminants material in many countries. Aniline create the reactive oxygen species (ROS) and cause to rise lipid hydroperoxide stages, damage of mitochondrial membrane, damage DNA and lead to variations in hepatocyte feasibility and apoptosis [7]. Also, the acute exposure aniline has toxic reaction in the spleen or liver and cause to splenomegaly, hyperplasia, fibrosis, and cancers with chronic exposure [8]. The toxicity and carcinogenicity of aniline was reported by NIOSH and OSHA [9–11]. The acute toxicity of aniline caused to convert to 4-hydroxyaniline and the formation of aniline compound with hemoglobin (Hb). In erythrocytes(RB), this is associated with the release of iron (Fe) and the accumulation of methemoglobin (MHb) and the development of hemolytic anemia and inflammation of the spleen. Tumor formation is often observed in the spleen on prolonged administration. The International Agency for Research on Cancer (IARC) classifies aniline as a group 2B carcinogenic compound owed to its mutagenic and carcinogenic possible [12] and the concentration of aniline must be evaluated in water samples. So the removal of aniline compounds from wastewater is mainly important for human health and eco-friendly protection. The analytical techniques include, gas chromatography [13], Spectrofluorimetry [14], the capillary zone electrophoresis (CZE) with field-enhanced sample injection [15,16] and high performance liquid chromatography (HPLC) [17] were used for the determination of aniline and derivatives in real samples. The different method include adsorption, the biological degradation, the catalytic oxidation

and the electrochemical procedure was used for eliminating aniline compounds from waters [18–20]. Due to toxicity of aniline and its derivatives, the aniline value must directly evaluate in water sources. As low concentration of aniline compounds in water samples, the pretreatment/preconcentration of the samples was used before analysis by HPLC, GC and liquid chromatography-tandem mass spectrometry [21]. Conventional techniques such as, adsorption, extraction, the chemical oxidation, the catalyzed process the electrochemical, the enzymatic process and the irradiation reported for anilines separation and determination in water samples. You et al. developed a new enzymatic method for the removal of aromatic pollutants from wastewaters by peroxidases [22, 23]. On the other hands, adsorbents such as graphene, graphene oxide, carbon nanotubes, MOF and silica with different physical and chemical properties were used for extraction/adsorption anilines from waters. In this study, the MHM-ACNPs nanoparticles were used for extraction aniline from waters by dispersive ionic liquid solid phase extraction procedure (D-IL-SPE). By procedure, the aniline adsorbed on nanostructure (MHM-ACNPs-COO.... NH-C<sub>6</sub>H<sub>5</sub>) at optimized pH. Then, aniline desorbed from MHM-ACNPs/IL by changing pH and determined by GC-FID.

## 2. Experimental

### 2.1. Apparatus

Agilent Gas chromatography with flame ionization detector (GC-FID) and mass detector (GC-MS) based on sample air loop injection (Windows XP Professional) was used (7890A, Netherland). This model of GC based on different detectors and equipped with a split injector was used for aniline analysis. A Hamilton syringe was used for the sample injected to the GC injector. The temperature of the injector tuned for the vaporization of aniline up to 185–200°C. The temperature of the injector port and detector of GC was tuned up to 200°C and 250°C, respectively. The oven temperature was tune up to 120°C and the flow rate of 1.5 mL min<sup>-1</sup> for H<sub>2</sub> was adjusted. The sample liquid was

**Table 1.** Gas chromatography conditions (Agilent, 7890A)

Parameters	Values
Injection Volume	1-10 $\mu$ L
Split ratio	2:1
Column	30 meter, 0.32mm x 0.25 $\mu$ m
Temperature Injector	200 °C
Detector FID	250 °C
Program	30 to 100 °C @ 25 °C/min,
Carrier Gas	H <sub>2</sub> @ 1.5 mL min <sup>-1</sup>
Gas Makeup	N <sub>2</sub> @ 30 mL min <sup>-1</sup>
Retention Time N,N-Dimethylaniline	18.1 (min)
Retention Time Aniline	10.9 (min)
Flow Rate N <sub>2</sub>	28 (mL min <sup>-1</sup> )
Flow Rate detector H <sub>2</sub>	60(mL min <sup>-1</sup> )
Flow Rate air	450(mL min <sup>-1</sup> )

injected into a GC injector with high temperature for vaporizing aniline. The liquids samples inject based on valves to the GC column (0.32 mm × 0.25  $\mu$ m). The pressures for inlets and detectors tuned between 35-100 psi for hydrogen with FID detector. The GC-MS was used for validation of aniline results which were adsorbed on MHM-ACNPs adsorbents. The conditions of GC were presented in [Table 1](#).

## 2.2. Reagents

The epoxy resin powders from waste printed circuit boards (WPCB) were provided by Shan- dong Zhonglv Eco-recycle Co. Ltd, China. According to our previous study [10], epoxy resin of WPCBs has low ash content (7%), water ratio (3%), high volatile matter (67%) and fixed carbon (23%). The carbon was measured by an energy dispersive spectrometer instrument (C: 42.16%). Aniline is an aromatic amine that may be used as a reactant in the synthesis of organic intermediates such as pyridine amine, phenyl amine and phenyl benzamide. So the pure Aniline prepared (CAS N: 62-53-3) from Sigma Aldrich. Hydrophobic ionic liquid 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (C<sub>11</sub>H<sub>20</sub>F<sub>6</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>, 223437-11-4) with density of 1.4 g cm<sup>-3</sup> and low solubility in water was used

for collecting of nanoparticles from liquid phase. Acetone, nitric acid and HCl were purchased from Merck, Germany. Ultrapure water was obtained from Millipore Water System (USA), The phosphate buffer (H<sub>2</sub>PO<sub>4</sub>/ HPO<sub>4</sub>) and ammonium buffer (NH<sub>3</sub>/ NH<sub>4</sub>Cl) prepared from Sigma an used for adjusting pH between 6.0–8.2 and 8-9, respectively.

## 2.3. Synthesis of adsorbent

### 2.3.1. Carbonization

Activated carbons (ACs) was synthesized by the carbonized method for 2.0 h at 600 °C by activating at 800 °C for 1 h in a furnace. The carbonized chars followed by typically heats biomass feedstock in a kiln (pyrolysis) at temperatures between 300-800°C in the absence of air. The produced also known as charcoal (porous and carbon-enriched). The carbonization furnace was used for the carbonization. Firstly, 20 g of raw powders prepared and placed in the porcelain crucible, then heated up to 600°C per minute and hold for 2.0 hours. By decreasing temperature up to 25°C, the product is ready for weight [24].

### 2.3.2. MHM-ACNPs Synthesis

The activation of ACs based on microwave heating method caused to create the MHM-ACNPs by previous works [24-26]. First, the

carbonized sample was mixed with KOH (CS/KOH; ratio 1:3; wt/wt). By the simple heating, the activation of CS/KOH (ACNPs) was carried out at 800 °C (rate: 25 °C min<sup>-1</sup>; hold: 1h) in a tube furnace and cooling down to room temperature under N<sub>2</sub> flow (0.5 Lmin<sup>-1</sup>). In the microwave heating method, the MHM-ACNPs were achieved by microwave furnace at a frequency of 2.45 GHz [25]. The mixture of CS/KOH was placed in the microwave furnace (800 W) and heated for 12 min [26]. The product was cooled up to 25°C under N<sub>2</sub> flow (0.5 Lmin<sup>-1</sup>). The MHM-ACNPs were washed with 10% HCl and then washed with DW up to pH=7.

#### 2.4. Extraction procedure for aniline

Due to D-IL-SPE method, the acetone, ionic liquid and MHM-ACNPs added to 100 mL of water samples at pH=8. After extraction, the concentration of aniline determined by GC-FID. Firstly, 30 mg of MHM-ACNPs added to mixture of acetone (1 mL) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (0.3 g) and then injected to water and standard solution of aniline (2.0 µg L<sup>-1</sup> and 950 µg L<sup>-1</sup>). After sonication for 10 min, the benzene ring in aniline as electron acceptor was chemically adsorbed on carboxylic

groups of MHM-ACNPs as electron donors (MHM-ACNPs-COO<sup>-</sup>.....C<sub>6</sub>H<sub>5</sub>-NH<sub>2</sub>). The MHM-ACNPs trapped in 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and separated from the liquid phase in the bottom of the conical tube after centrifuging (3.5 min; 4000 rpm). The upper of the liquid sample was removed and then, the aniline back-extracted from MHM-ACNPs in acidic pH (HNO<sub>3</sub>, 0.3 mol L<sup>-1</sup>). After shaking and centrifuging, the remained solution diluted up to 0.5 mL with DW and determined by GC-FID (Fig. 1). The procedure was used for a blank experimental run without any aniline for ten times. The calibration curve for aniline in standards solutions was prepared based on D-IL-SPE/GC-FID procedure (2.0- 950 µg L<sup>-1</sup>) and GC-FID method (0.4- 800 mg L<sup>-1</sup>) and preconcentration factor (PF) calculated by curve fitting of calibration curves (m<sub>1</sub>/m<sub>2</sub>). Each sample was analyzed separately by means of a GC-FID. The aniline was detected with a FID detector. Aniline (mol) were calculated by the following Equations (1) as extraction efficiency and Equations (2) as recovery,

$$\%EE = [\text{Initial aniline} - \text{Final aniline} / \text{Initial aniline}] \times 100 \quad (1)$$

$$\% \text{Recovery} = \text{Final aniline amount (mol)} / \text{Initial aniline amount (mol)} \times 100 \quad (2)$$

### 3. Results and Discussion

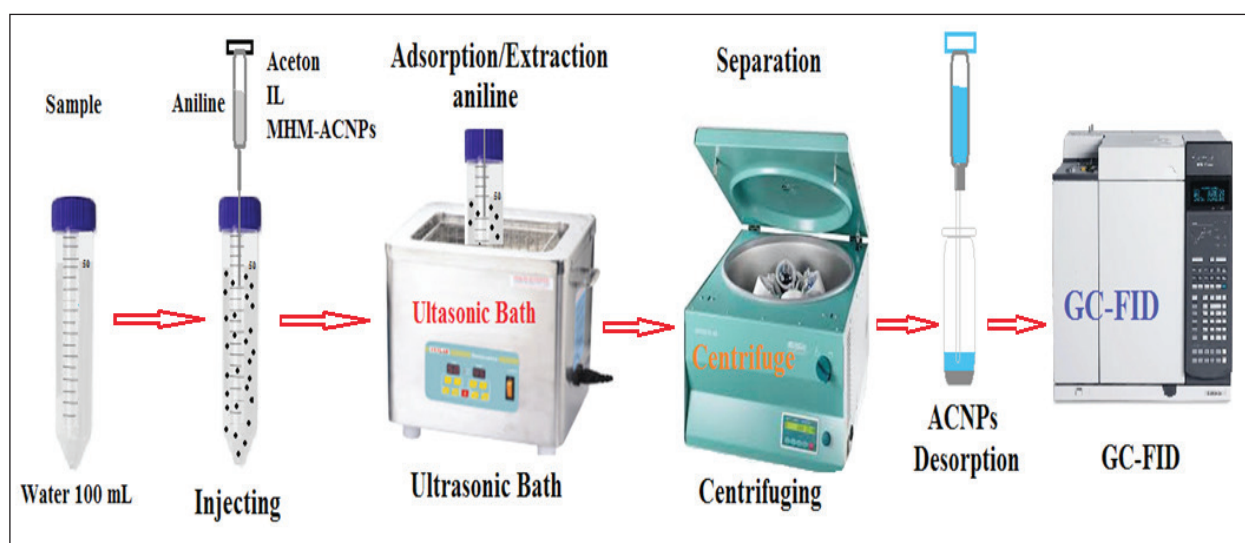


Fig. 1. The extraction procedure for aniline in waters by MHM-ACNPs and GC-FID

The FTIR showed that the MHM-ACNPs with high surface area ( $2792 \text{ m}^2 \text{ g}^{-1}$ ) and function groups can be efficiently absorbed/extracted the aniline ( $\text{NH}_2\text{-C}_6\text{H}_5$ ) in water samples as compared to ACs. For optimizing, the important parameters on aniline extraction such as, pH, amount of ionic liquid, sample volume, amount of sorbent, amount of IL, shaking time were studied.

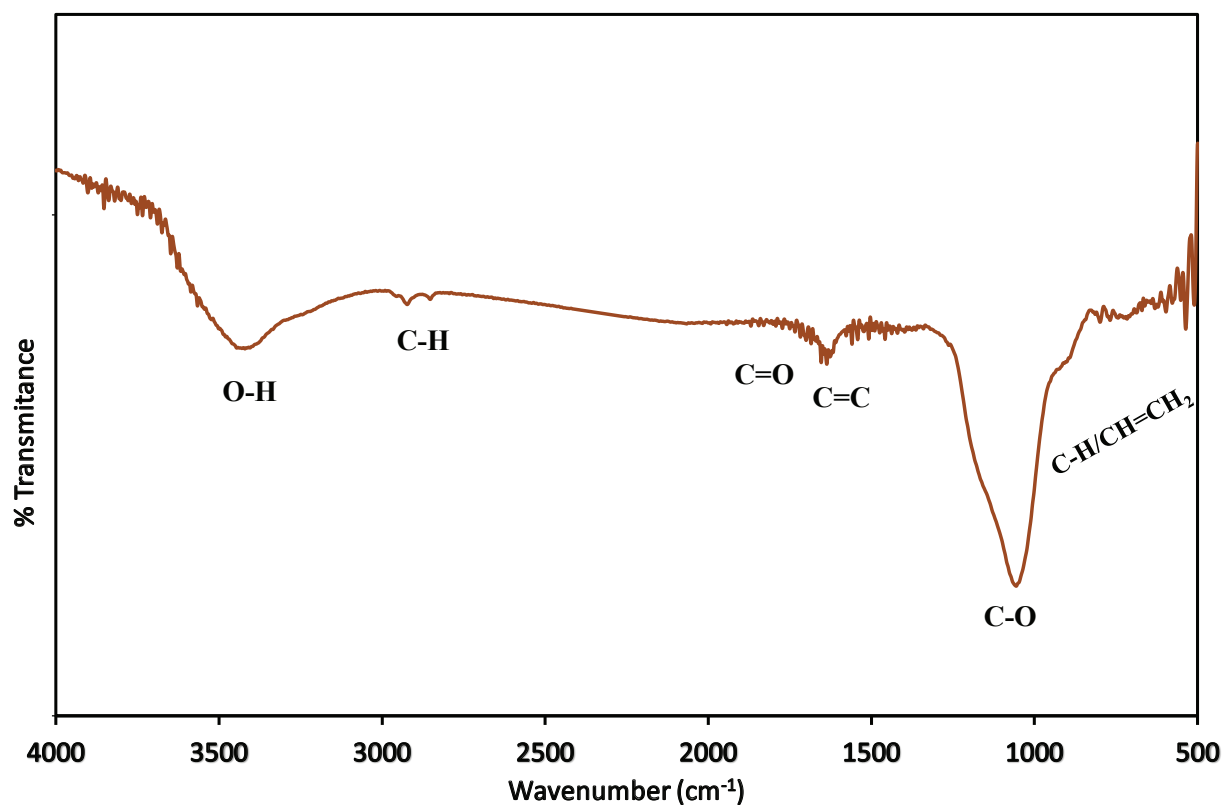
### 3.1. FTIR of MHM-ACNPs

The FTIR spectrum of MHM-ACNPs is illustrated in **Figure 2**. The band at around  $3428 \text{ cm}^{-1}$  was attributed to the stretching vibration of hydroxyl. The  $2910$  and  $2840 \text{ cm}^{-1}$  bands were respectively assigned to asymmetric and symmetric C-H stretching vibration of methylene. The vibration band at  $1710 \text{ cm}^{-1}$  was identified as C=O stretching mode of carboxylic groups, while the peak at  $1058 \text{ cm}^{-1}$  was corresponded to the C-O vibration. The

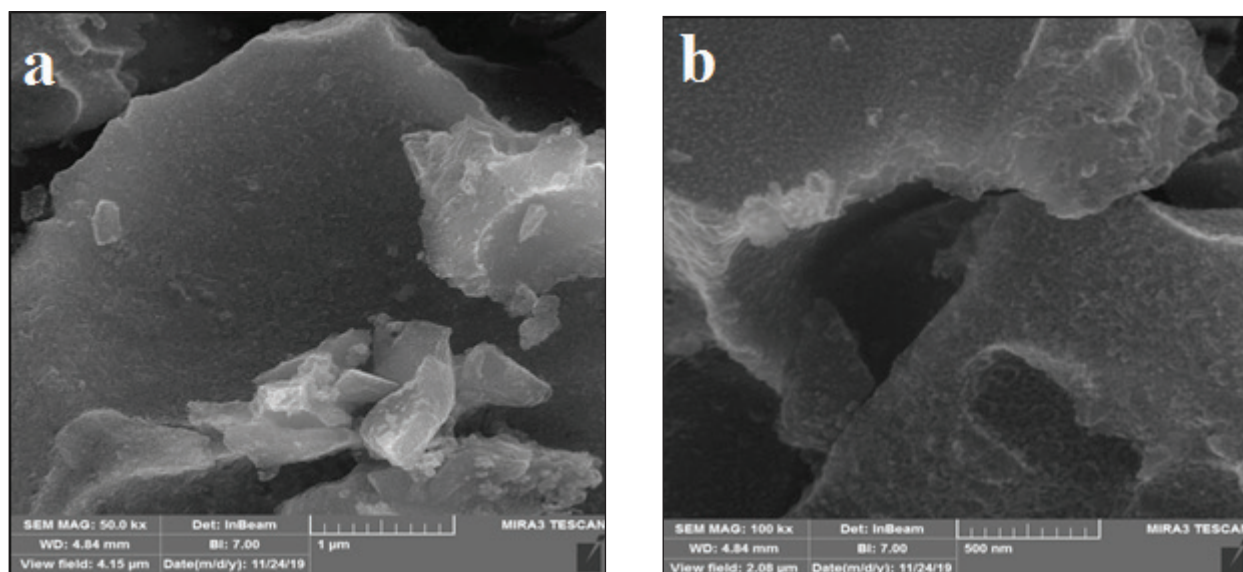
peak at  $1613$  is characteristic of stretching vibration of C=C in benzene rings. A group of bands can be seen between  $850$  and  $500 \text{ cm}^{-1}$ , which are ascribed to C-H and  $\text{CH=CH}_2$  vibrations in aromatic rings.

### 3.2. SEM and TEM of MHM-ACNPs

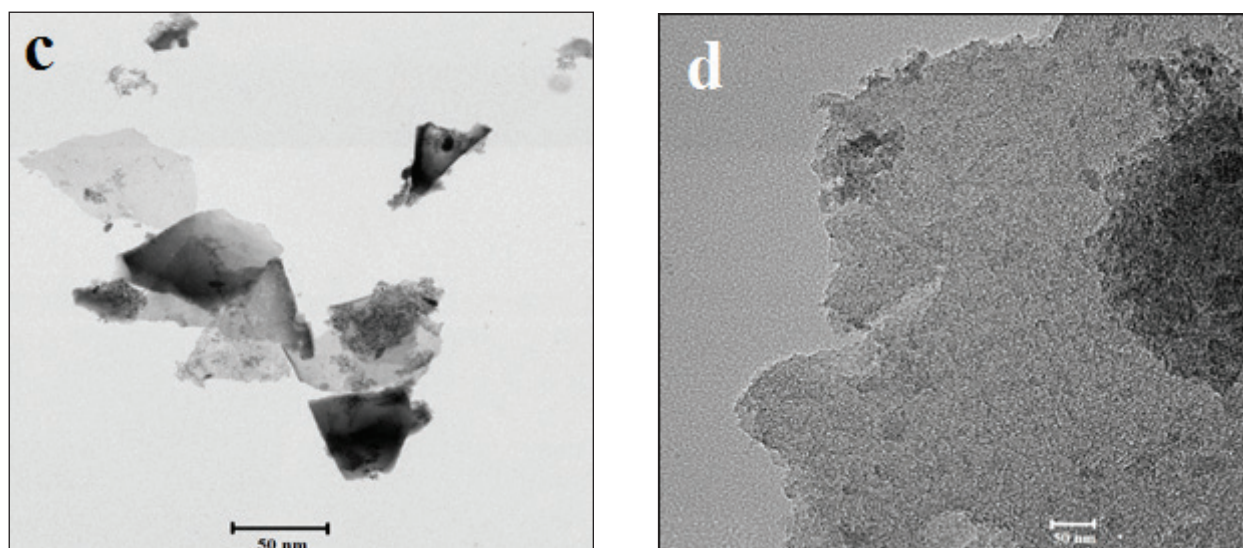
HR-SEM and HRTEM were used for morphological study of prepared MHM-ACNPs (**Fig. 3**). **Figure 3a** and **b** illustrates the FE-SEM images of the synthesized MHM-ACNPs sample. The FE-SEM images of MHM-ACNPs sample displayed small broken pieces of particles with irregular shapes, which can significantly affect the pore characteristics (e.g., pore size distribution and average pore diameter). From **Figure 3b**, MHM-ACNPs appeared to have many different sizes of pores, indicating that the structure had been destroyed and a dense porosity was formed through KOH activation. In order to observe the structure of MHM-ACNPs anoadsorbents, HR-



**Fig. 2.** The FTIR spectrum of MHM-ACNPs adsorbent



**Fig. 3.** (a) the FE-SEM images of the synthesized MHM-ACNPs (b) different sizes of pores



**Fig.3.** (c)The HR-TEM image of MHM-ACNPs by 2D morphology (d) The HR-TEM image of MHM-ACNPs with intermittent graphitic layers and porous structure

TEM imaging was employed. The HR-TEM image (**Fig. 3c**) clearly shows the graphene-like structure with a 2D morphology, and the image with 50 nm scale (**Fig. 3d**) confirms the existence of intermittent graphitic layers and porous structure.

### 3.3. Optimizations of parameters for extraction aniline

The D-IL-SPE procedure based on MHM-ACNPs nanocomposite was used for extraction of aniline ( $\text{NH}_2\text{-C}_6\text{H}_5$ ) from water and wastewater samples. The main effectiveness parameters such as, pH, amount

of MHM-ACNPs, amount of ionic liquid, sonication time, volume of samples, adsorption capacity of sorbent were evaluated and studied. The mechanism of adsorption depended on the benzene ring in aniline. The benzene ring as electron acceptor was adsorbed on carboxylic groups of sorbent as electron donors ( $\text{R-COO}^-\text{.....C}_6\text{H}_5$ ). After extraction, the sorbent/aniline was collected by 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide as a hydrophobic ionic liquid phase in bottom of conical centrifuging tube.

#### 3.3.1. pH effect on aniline extraction

The pH sample is critical factor for aniline extraction in water samples and must be studied. The efficient extraction of aniline based on MHM-ACNPs depended on pH value of water samples which was optimized by D-IL-SPE methods. The pH range from 2 to 11 was examined with different buffer solution and the recovery of aniline extraction in water samples was evaluated in presence of aniline concentration between  $2.0\text{--}950\text{ }\mu\text{g L}^{-1}$  for 30 mg of MHM-ACNPs. Based on results, the extraction of aniline was reduced at acidic pH ( $\text{pH}<6$ ) and pH of 7-9 had more extraction for aniline in waters (Fig. 4). So, in this study, the pH of 8.0 was selected as optimized pH for aniline extraction in waters.

### 3.3.2. The effect of MHM-ACNPs adsorbent on aniline extraction

By proposed method, the amounts of on MHM-ACNPs adsorbent for 100 mL of water and wastewater samples were evaluated. Therefore, the amount of 5-50 mg of MHM-ACNPs and AC was used by D-IL-SPE procedure. The results showed us, aniline efficiently extracted by 25 mg MHM-ACNPs in  $\text{pH}=8$ . So, the amount of 30 mg of MHM-ACNPs adsorbent was selected for aniline extraction in water samples (Fig. 5).

### 3.3.3. The effect of sample volume on aniline extraction

The sample volume as an important factor for aniline extraction in water samples. For this proposed, the effect of sample volume for extraction of aniline in waters was evaluated. By procedure, the various sample volumes between 20-150 mL was used for optimizing volume in presence of  $2.0\text{--}950\text{ }\mu\text{g L}^{-1}$  of aniline concentration for 30 mg of MHM-ACNPs. The results showed, high recovery obtained for 120 mL of waters. Therefore, 100 mL of sample volume selected for further studies (Fig. 6).

### 3.3.4. The adsorption capacity

For evaluating of reusability of MHM-ACNPs, the nanoparticles of adsorbent were dispersed in water samples and used for aniline extraction for many times by the D-IL-SPE procedure. The experimental results showed, the aniline was efficiently extracted with MHM-ACNPs adsorbent for 19 cycles of extraction at  $\text{pH}=8.0$ . So, the MHM-ACNPs adsorbent can be used for 17 extractions/back-extraction steps for aniline in waters. The absorption capacities of adsorbents depended on the structure, surface area (SA) and nanoparticle size (NS) in different samples. For calculating of the absorption capacities, 30 mg of MHM-ACNPs

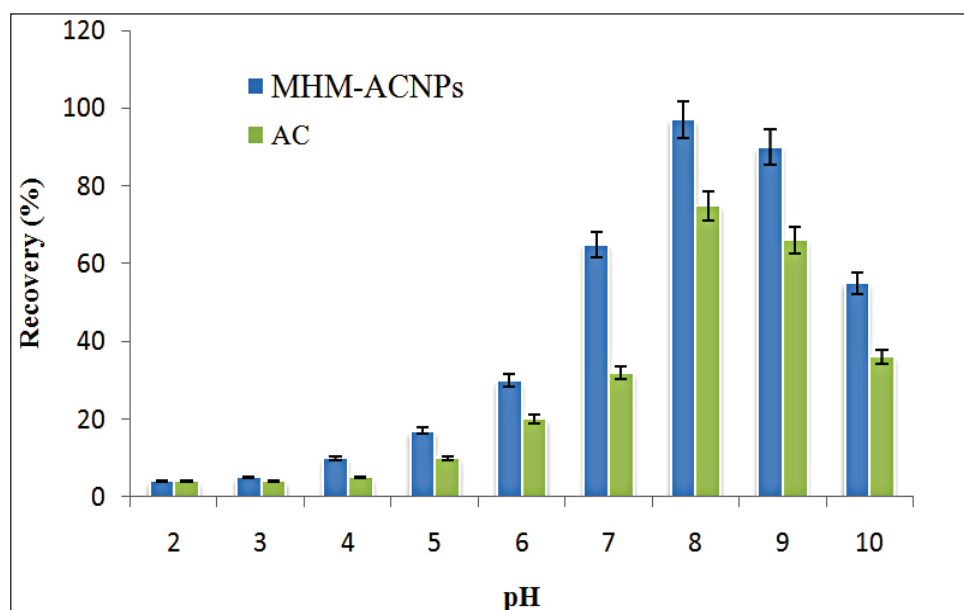
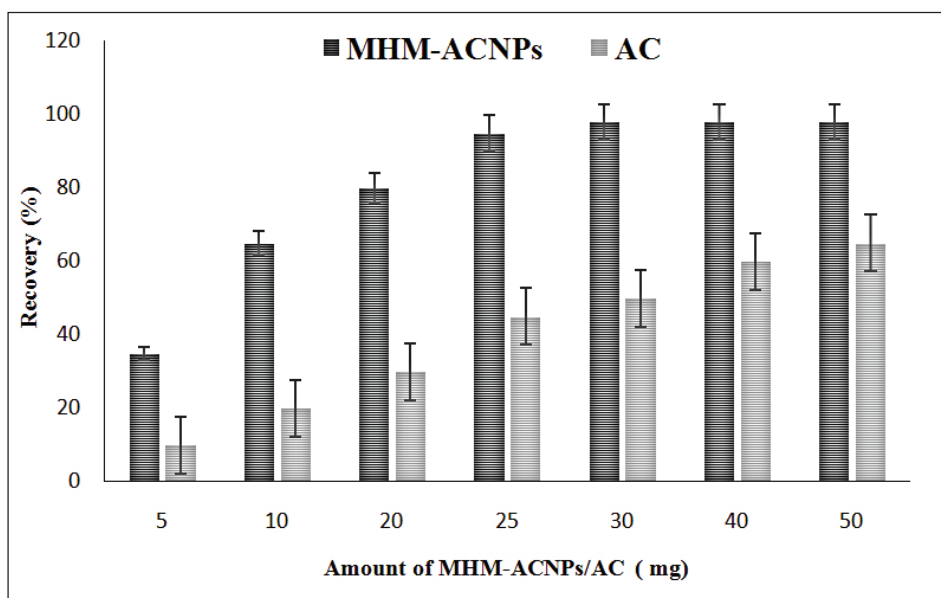
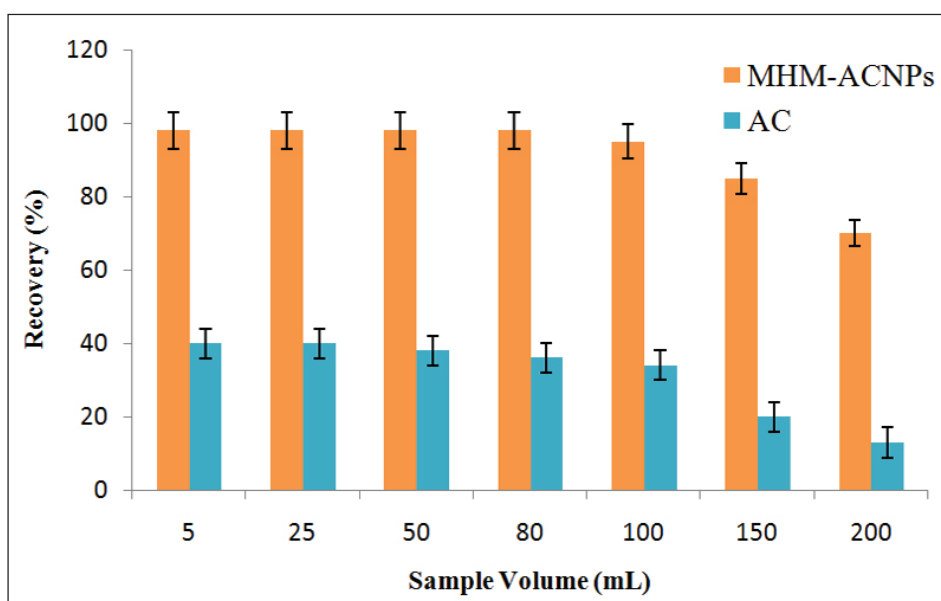


Fig. 4. The effect of pH on aniline extraction by MHM-ACNPs and AC adsorbents from water samples



**Fig. 5.** The effect of MHM-ACNPs and AC adsorbents on aniline extraction by D-IL-SPE method



**Fig. 6.** The effect of sample volume on aniline extraction by MHM-ACNPs and AC adsorbents

and AC nanoparticles was added to 100 mL of water samples with 20 mg L<sup>-1</sup> (ppm) of aniline concentration at pH of 8.0. After 30 min sonication, the aniline was extracted by MHM-ACNPs and AC in solutions. Finally, the concentrations of aniline directly determined in remain solution by GC-FID. The adsorption capacities of the MHM-ACNPs and AC structure for aniline were achieved 155.8 mg g<sup>-1</sup> and 77.2 mg g<sup>-1</sup>, respectively in water samples.

### 3.3.5. Aniline validation in real samples

The MHM-ACNPs adsorbent was used for determination and extraction aniline in water and wastewater samples. The experimental results showed, the aniline was efficiently extracted with proposed procedure and validated by spiking of real samples (**Table 2**). The validation of the results were obtained by spiking of water samples with a standard aniline at pH=8.0.

The extraction efficiency of spiked samples demonstrated that the MHM-ACNPs adsorbent was satisfactory results for aniline extraction and determination in water and wastewater samples at pH of 8.0. Moreover, the GC-MS were used for validating of methodology based on MHM-ACNPs adsorbent and IL by the D-IL-SPE procedure (**Table 3**). Also, the aniline extraction based on MHM-ACNPs adsorbent by the D-IL-SPE procedure was compared to other adsorbent and technology which was shown in **Table 4**.

### 3.3.6. Discussion

Recently, the aniline was removed/extracted from different matrixes by various technologies by researchers. They showed the different adsorbent and techniques for extraction aniline from water and wastewater samples and the various analytical parameters such as, LOD, LOQ, linear range, RSD% and absorption capacities reported which was shown in **Table 4**. Kakavandi et al were used the Fe<sub>3</sub>O<sub>4</sub>-activated carbon magnetic nanoparticles (AC-Fe<sub>3</sub>O<sub>4</sub>MNPs) for extraction

**Table 2.** Validation of the D-IL-SPE/GC-FID procedure for determination of aniline in water and wastewater samples by spiking of standard solutions

Sample	Added ( $\mu\text{g L}^{-1}$ )	*Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)
Tap water	-----	$4.24 \pm 0.22$	-----
	5	$9.31 \pm 0.24$	101.4
Drinking water	-----	ND	-----
	10	$9.82 \pm 0.46$	98.2
Well water	-----	$19.54 \pm 0.95$	-----
	20	$38.98 \pm 1.84$	97.2
wastewater	-----	$335.92 \pm 15.11$	-----
	300	$628.33 \pm 27.65$	97.5
Wastewater	-----	$188.60 \pm 8.75$	-----
	200	$379.70 \pm 16.40$	95.6

\* $\bar{x} \pm ts / \sqrt{n}$  at 95% confidence (n=5)

**Table 3.** Validation of the D-IL-SPE/GC-FID procedure for determination of aniline in water and wastewater samples by GC-MS

Sample	Added ( $\mu\text{g L}^{-1}$ )	GC-MS ( $\mu\text{g L}^{-1}$ )	* D-IL-SPE/GC-FID ( $\mu\text{g L}^{-1}$ )	Recovery (%)
Water A	-----	$11.35 \pm 0.28$	$10.96 \pm 0.53$	96.6
	10	-----	$20.78 \pm 0.24$	98.2
Water B	-----	$53.14 \pm 0.57$	$53.78 \pm 2.44$	101.2
	50	-----	$102.66 \pm 4.82$	97.8
Water C	-----	$98.53 \pm 1.67$	$101.03 \pm 5.12$	102.5
	100	-----	$199.87 \pm 9.34$	98.8
Water D	-----	$202.38 \pm 4.12$	$195.82 \pm 10.13$	96.8
	200	-----	$400.08 \pm 18.52$	102.1

\* $\bar{x} \pm ts / \sqrt{n}$  at 95% confidence (n=5)

**Table 4.** Comparison of proposed procedure with other published methods

Adsorbent	Matrix	Method	Linear range	Instrument	Recovery (%)	References
C8-column	Water	ESI	0.05- 2 $\mu\text{g L}^{-1}$	LC- MS/MS	99-102%	[27]
AC-Fe <sub>3</sub> O <sub>4</sub> MNPs	Water	Adsorbent	50-300 $\text{mg L}^{-1}$	XRD,SEM,TEM	21.1-99%	[28]
Soybean peroxidase	Wastewater	Enzymatic	-----	UV-Vis	95%	[29]
-----	Water	NIAA	50–1000 $\mu\text{g L}^{-1}$	CZE	93-104%	[30]
Activated carbon (AC)	Wastewater	Enzymatic	20-600 $\text{mg L}^{-1}$	UV-Vis	89–94%	[31]
MFH nanocomposites	Wastewater	Electrostatic	50-200 $\text{mg L}^{-1}$	XRD	95.1%	[32]
PFPA	PAAW	Extraction	0.03–1.4 $\mu\text{g L}^{-1}$	UHPLC-MS/MS	21–110%	[33]
MHM-ACNPs	Water	Adsorption	2.0-950 $\mu\text{g L}^{-1}$	GC-FID/D-IL-SPE	95-102%	This work

NIAA: Non-ionic or anionic analytes

CZE: Capillary zone electrophoresis

PFPA: Mobile phases perfluoropentanoic acid (PFPA) in water and methanol

PAAW: Primary aromatic amines (PAAs) in Water

of aniline in waters and the characterization of AC-Fe<sub>3</sub>O<sub>4</sub>MNPs adsorbent obtained by SEM, TEM, XRD, and BET [28]. Also, the results were showed by two kinetic models for adsorption of AC-Fe<sub>3</sub>O<sub>4</sub>MNPs (Langmuir and Freundlich). The linear range and recovery were achieved 50-300  $\text{mg L}^{-1}$  and between 21.1-99%, respectively. Rahdar et al were presented a novel magnetic Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanocomposite (Fe@SiNPs) for removal aniline from waters by an electrochemical method. Due to the special characterization of Fe@SiNPs nanocomposite such as, vibrating-sample magnetometry (VSM), XRD, SEM, and FT-IR, the extraction recovery of 71% was obtained. The physical and chemical properties of Fe@SiNPs adsorbent caused to efficient extraction of aniline from the water samples. By optimizing paramours, 50 mg of Fe@SiNp can be removed aniline in waters with absorption capacity of 126.6  $\text{mg g}^{-1}$  at pH 6 (50°C) which was lower than the proposed D-IL-SPE procedure. The adsorption of aniline by Fe@SiNp is fast and exothermic which was shown by the kinetic model ( $r^2 = 1$ ) and the Freundlich isotherm model ( $r^2 = 0.9986$ ) [34]. In another study, the polyaniline (PANI)

grafted MWCNTs (PANI/MWCNTs) was used for extraction of aniline in water samples. PANI/MWCNTs were characterized by using ultraviolet–visible spectrophotometry (UV-VIS), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy (RS), the differential thermal analysis (DTA), the differential scanning calorimetry (DSC), and field-emission scanning electron microscopy (FE-SEM). The maximum removal of PANI/MWCNTs adsorbent was achieved around 99% for aniline in waters [35]. Based on our study, the MHM-ACNPs were used for fast, simple and efficient extraction aniline from waters by dispersive ionic liquid solid phase extraction procedure (D-IL-SPE). The aniline adsorbed on nanostructure (MHM-ACNPs -COO.... C<sub>6</sub>H<sub>5</sub>) with high absorption capacity, the recovery and the extraction as compared to other methods. After back-extraction of aniline, the concentration of aniline is determined by GC-FID and validated by GC-MS. The wide working range was obtained from 2.0 to 4000  $\mu\text{g L}^{-1}$  (RSD% < 1.8) which was higher than other published methods. Based on Table 4, the LOD, PF and linear ranges is better than other presented methods.

#### 4. Conclusions

In this study, a robust procedure based on MHM-ACNPs adsorbent was used for the aniline extraction from water samples. The MHM-ACNPs/aniline was simply separated/collected from water samples in bottom of conical tube by hydrophobic 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide. By D-IL-SPE procedure, the efficient extraction, good preconcentration, and the perfect sample preparation was obtained in optimized conditions. By the mixture of IL/ MHM-ACNPs /acetone, the high recovery between 95-102% for aniline extraction were achieved in short time. The developed D-IL-SPE procedure had many advantages such as, the favorite reusability, low LOD and RSD% with accurate and precise results. Therefore, the aniline can be efficiently extracted in water samples based on MHM-ACNPs adsorbent by D-IL-SPE /GC-FID procedure.

#### 5. Acknowledgements

The authors wish to thank from Chemistry Department, Yasouj University, Yasouj, Iran and Islamic Azad University, Bandar Abbas Branch, Iran

#### 6. References

- [1] F. K. Mostafapoor, Sh. Ahmadi, D. Balarak, S. Rahdar, Comparison of dissolved air flotation process function for aniline and penicillin G removal from aqueous solutions, *Hamadan Un. Med. Sci.*, 82 (2016) 203-209.
- [2] U.S.EPA, Environmental Protection Agency, health and environmental effects profile for aniline. office of health and environmental assessment, office of research and development, Cincinnati, OH., 1985.
- [3] J.G. Cai, A. Li, H.Y. Shi, Z.H. Fei, C. Long, Q.X. Zhang, Adsorption characteristics of aniline and 4-methylaniline onto bifunctional polymeric adsorbent modified by sulfonic groups, *J. Hazard. Mater.*, 124 (2005) 173-180.
- [4] T. Kahl, K.W. Schröder, F.R. Lawrence, W.J. Marshall, H. Höke, R. Jäckh, Aniline, in Ullmann, Fritz (ed.). *Ullmann's encyclopedia of industrial chemistry*. John Wiley & Sons: New York, 2007. [http://doi:10.1002/14356007.a02\\_303](http://doi:10.1002/14356007.a02_303).
- [5] H. Ma, J. Wang, S.Z. Abdel-Rahman, T.K. Hazra, P.J. Boor, M.F. Khan, Induction of NEIL1 and NEIL2 DNA glycosylases in aniline-induced splenic toxicity, *Toxicol. Appl. Pharmacol.*, 251 (2011) 1-7.
- [6] U. Khairnar, A. Upaganlawar, C. Upasani, Ameliorative effect of chronic supplementation of protocatechuic acid alone and in combination with ascorbic acid in aniline hydrochloride induced spleen toxicity in rats, *Scientifica (Cairo)*, 2016 (2016) 1-9.
- [7] H. Ma, J. Wang, S.Z. Abdel-Rahman, P.J. Boor, M.F. Khan, Oxidative DNA damage and its repair in rat spleen following subchronic exposure to aniline, *Toxicol. Appl. Pharmacol.*, 233 (2008) 247-253.
- [8] P. Makhdoumi, H. Hossini, Molecular mechanism of aniline induced spleen toxicity and neuron toxicity in experimental rat exposure, A review, *Curr. Neuropharmacol.*, 17 (2019) 201-213.
- [9] NIOSH, the pocket guide to chemical hazards, Department of health and human services (DHHS), centers for disease control and prevention, National institute for occupational safety and health (NIOSH), Cincinnati, OH. U.S., Publication No. 168c, 2010. <http://www.cdc.gov/niosh/npg/>.
- [10] OSHA, Hazard communication. final rule, Washington, DC. U.S. Department of labor, occupational safety and health administration, OSHA, 77 (2012) 17574-17896. [https://osha.gov/pls/oshaweb/owadisp.show\\_document/](https://osha.gov/pls/oshaweb/owadisp.show_document/).
- [11] T.J. Lentz, M. Seaton, P. Rane, S.J. Gilbert, L.T. McKiernan, C. Whittaker, Technical report, the occupational exposure banding process for chemical risk management, Department of health and human services (DHHS), centers for disease control and prevention

- (CDC), National institute for occupational safety and health (NIOSH), 2019. <https://doi.org/10.26616/NIOSH PUB2019132>.
- [12] IARC, Agents classified by the IARC monographs, the international Agency for research on cancer (IARC) Vol. 1–112, 2015. <http://monographs.iarc. /Classification/ClassificationsAlphaOrder.pdf>.
- [13] E. Ebrahimpour, A.h. Amir, Poly (indole-co-thiophene)  $\text{Fe}_3\text{O}_4$  as novel adsorbents for the extraction of aniline derivatives from water samples, *Microchem. J.*, 131 ( 2017) 174–181.
- [14] H. Bagheri, R. Daliri, A. Roostaie, A novel magnetic poly(aniline-naphthylamine)-based nanocomposite for micro solid phase extraction of rhodamine, *Anal. Chim. Acta*, 794 (2013) 38–46.
- [15] T. Hattori, H. Okamura, S. Asaoka, K. Fukushi, Capillary zone electrophoresis determination of aniline and pyridine in sewage samples using transient isotachopheresis with a system-induced terminator, *J. Chromatog. A*, 1511 (2017) 132–137.
- [16] S. Liu, W. Wang, J. Chen, J. Sun, Determination of aniline and its derivatives in environmental water by capillary electrophoresis with on-line concentration, *Int. J. Mol. Sci.*, 13 (2012) 6863–6872.
- [17] S. Boulahlib, A. Boudina, Development and validation of a fast and simple HPLC method for the simultaneous determination of aniline and its degradation products in wastewater, *Anal. Methods*, 8 (2016) 5949–5956.
- [18] V. Froidevaux, C. Negrell, S. Caillol, J.P. Pascault, B. Boutevin, Biobased amines: from synthesis to polymers, present and future, *Chem. Rev.*, 116 (2016) 14181–14224.
- [19] S. Tadrent, D. Luart, O. Bals, A. Khelfa, R. Luque, C. Len, Metal-free reduction of nitrobenzene to aniline in subcritical water, *J. Org. Chem.*, 83 (2018) 7431–7437.
- [20] N. Galy, R. Nguyen, H. Yalgin, N. Thiebault, D. Luard, C. Len, Glycerol in sub and supercritical solvents, *J. Chem. Technol. Biotechnol.*, 92 (2017) 14–26.
- [21] M.A. Favaro Perez, M. Padula, Primary aromatic amines in kitchenware: Determination by liquid chromatography-tandem mass spectrometry, *J. Chromatogr. A*, 1602 (2019) 217–227.
- [22] X. You, E. Li, J. Liu, S. Li, Using natural biomacromolecules for adsorptive and enzymatic removal of aniline blue from water, *Molecules*, 23 (2018) 1606.
- [23] S. Mazloun, M.M. Al-Ansari, K. Taylor, J.K. Bewtra, N. Biswas, Additive effect on soybean peroxidase-catalyzed removal of anilines from water, *Environ. Eng. Sci.*, 33 (2016) 133–139.
- [24] Y. Kan, Q. Yue, B. Gao, Q. Li, Preparation of epoxy resin-based activated carbons from waste printed circuit boards by steam activation, *Mater. Lett.*, 159 (2015) 443–446.
- [25] J.M. Valente Nabais, P.J.M. Carrott, M.M.L. Ribeiro Carrott, J.A. Menéndez, Preparation and modification of activated carbon fibers by microwave heating, *Carbon*, 42 (2004) 1315–1320.
- [26] L. Huang, Y. Sun, W. Wang, Q. Yue, T. Yang, Comparative study on characterization of activated carbons prepared by microwave and conventional heating methods and application in removal of oxytetracycline (OTC), *Chem. Eng. J.*, 171 (2011) 1446–1453.
- [27] K. Furukawa, M. Hashimoto, S. Kaneco, Optimization of analytical conditions for a rapid determination of aniline in environmental water by liquid chromatography/tandem mass spectrometry, *Anal. Sci.*, 33 (2017) 1189–1191.
- [28] B. Kakavandi, A.J. Jonidi, R.K. Rezaei, S. Nasser, A. Ameri, A. Esrafi, Synthesis and properties of  $\text{Fe}_3\text{O}_4$ -activated carbon magnetic nanoparticles for removal of aniline

- from aqueous solution, equilibrium, kinetic and thermodynamic studies, Iran. J. Environ. Health Sci. Eng., 10 (2013) 19.
- [29] S. Mazloun, M.M. Al-Ansari, K. Taylor, J.K. Bewtra, N. Biswas, Additive effect on soybean peroxidase-catalyzed removal of anilines from water, Environ. Eng. Sci., 33 (2016) 133-139.
- [30] S. Liu, W. Wang, J. Chen, J. Sun, Determination of aniline and Its derivatives in environmental water by capillary electrophoresis with on-line concentration, Int. J. Mol. Sci., 13 (2012) 6863-6872.
- [31] X. You, E. Li, J. Liu, S. Li, Using natural biomacromolecules for adsorptive and enzymatic removal of aniline blue from water, Molecules, 23 (2018) 1606.
- [32] H. Lu, J. Wang, F.F. Li, X. Huang, B. Tian, H. Hao, Highly efficient and reusable montmorillonite/Fe<sub>3</sub>O<sub>4</sub>/humic acid nanocomposites for simultaneous removal of Cr(VI) and aniline, Nanomater., 8 (2018) 537.
- [33] O. Yavuz, S. Valzacchi, E. Hoekstra, C. Simoneau, Determination of primary aromatic amines in cold water extract of coloured paper napkin samples by liquid chromatography-tandem mass spectrometry, Food Addit. Contam. Part A, 33 (2016) 1072-1079.
- [34] A. Rahdar, S. Rahdar, G. Labuto, Environmentally friendly synthesis of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> nanocomposite, characterization and application as an adsorbent to aniline removal from aqueous solution, Environ. Sci. Pollut. Res. Int., 27 (2020) 9181-9191.
- [35] D. Shao, J. Hu, C. Chen, G. Sheng, X. Ren, X. Wang, Polyaniline multiwalled carbon nanotube magnetic composite prepared by plasma-induced graft technique and its application for removal of aniline and phenol, J. Phys. Chem. C, 114 (2010) 21524-21530.