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Investigation of graphene/CNT hybrid structural effect on absorption of Mn²⁺ by activated carbon

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ABSTRACT

In this paper, an effort is made to improve the adsorption amount by adding graphene/CNT hybrid in the structure of activated carbon (AC) for removing manganese ions from aqueous solutions. The bonding G/CNT hybrid with activated carbon creates a structure which is an excellent absorbent for removing some heavy metal ions. Therefore, a comparison between the performance increasing ion adsorption and AC results as the blank adsorbent was made. Moreover, the influence of time, pH solution, initial concentration of Mn²⁺, and temperature investigated as experimental conditions. Finally, the maximum adsorption was 89.38% and 96.18% for AC and AC/G/CNT composite respectively at 30 min, initial concentration of 30 mgL⁻¹, pH=4.5 in 15 °C for both adsorbents. Finally, the results showed that under the same conditions, the presence of G/CNT hybrid in the structure of AC increased the amount of adsorption by 7.5%.

1. Introduction

Heavy metal ions and organics are two major classes of water pollutants. Heavy metal (a range of toxic metals) ions as poisonous compounds are one of the main problems that pollute the waters and plants. Discharging of pollutant water in plants will be absorbed in soil and will not degrade and accumulate in living organisms, causing various poisoning problems in animals and indirection for humans. Therefore, elimination of these heavy metal ions from waste water is necessary and interest [1].

*Corresponding Author. Ahmad Ghozatloo E-mail: ghozatlooa@ripi.ir https://doi.org/10.24200/amecj.v2.i2.60 Moreover, the major techniques have been used to reduce or decrease the heavy metal ions from wastewaters such as flotation, solvent extraction, silica, adsorption processes, ion exchange, reverse osmosis, lime chemical precipitation and coagulation [2]. Among these, adsorption is an industrial and good method for removing heavy metals from aqueous solutions [3]. Copper (Cu), mercury, cadmium, manganese (Mn²⁺), nickel, chromium and lead are known to be greatly toxic effect on waters [4]. The ion of Mn²⁺ can be found in the effluents of petrochemical plants is one of dangers source of pollution. In addition, pore structure of some substances which have active surface such as chitosan, anthracite, lignite, and specially activated carbon (AC) are common and suitable for adoption Mn²⁺ and widely used for high adsorption capacity [5]. The objective of this paper was to improve performance of AC by G/CNT structures. Because the multi-layer configuration of graphene/CNT (G/CNT) hybrid structure is to have good adsorption performance, so recently, graphene hybrid structure has been applied as the adsorbent for absorption of some pollutants from waste water, because of its excellent capacitance. To improve interface and chemistry surface behavior, wide researches have been conducted on the structure of G/CNT hybrid structures [6]. In this paper, the effects of temperature, time, pH, and initial Mn²⁺ concentration were investigated to remove the cations of Mn²⁺ from water by AC/G/ CNT composite as adsorbent and comparison with AC.

2. Material and Methods

The chemicals used for this paper were all Merck grade and used without further purification. Analytical grade of AC Powder was obtained from activated charcoal with the purity of > 99.9%. The solutions were prepared in deionized water. The Synthetic aqueous solutions of Mn^{2+} were prepared by dissolving enough amount of $Mn(NO_3)_2$ in pure water. In order to prepare the aqueous solutions with various concentrations, first a stock solution was prepared with a concentration of 1000 mg/L of Mn^{2+} . For this purpose, 0.65 g of $Mn(NO_3)_2$ was introduced in 1000 mL volumetric flask, added adequate water, and stirrer the solution. Then

the purposed solutions were prepared with lower concentrations by dilution.

2.1. Preparation of activated carbon

First, 200 g of powdered glucose are placed in a tubular quartz reactor into the furnace under nitrogen atmosphere for 30 min. It is then gently warmed up to a temperature of 350 °C and remains for 2 hr. The glucose is carbonized under these conditions and is colored as a black powder. The powder placed in a furnace and heated at 400 °C for 1 hr under neutral atmosphere. Next the powder was extracted from the reactor and poured into 1 molar HCl at 90 °C for 30 min. The remaining mixture is filtered and washed with distilled water several times. Afterwards, the filter cake was dried in oven 65 °C for 11 hr. Dried powder is a activated carbon that is susceptible to participation in the carbon nanostructures.

2.2. Synthesis of AC/G/CNT composite

To synthesis of Graphene/CNT hybrid (G/CNT hybrid) a two-step method of chemical vapor deposition (CVD) was used. Its mechanism includes copper sheets by FeMo nanoparticles (as a catalyst) in the space of interlayer of copper sheets to formation of CNT/Graphene nanostructure as illustrated in figure 1.

According to figure 1 in the section (a), metal NPs nucleated on the surface of copper sheets as activated catalyst for growth of CNT. Section (b) is as first step of G/CNT hybrid synthesis which CNT fully grown on copper sheets by FeMo in 600 °C as low temperature process CVD catalyst



Fig. 1. Schematic illustration synthesis of G/CNT hybrid.

1	1		
Independent Variables	-1 level	0 level	+1 level
Mn^{+2} conc. (mgL ⁻¹)	30	80	130
Temperature (°C)	15	25	35
Time (min)	15	30	45
pH	3.5	4.5	5.5

Table 1. The levels of independent variables process.

and section (c) is as second step of G/CNT hybrid synthesis which uniform Graphene nanosheets deposited on copper for G/CNT hybrid formation as higher temperature process. Finally, in section (d), acid washing was done to remove FeMo, copper sheets and other pollutants from G/CNT hybrid structure to obtain the high carbon purity [7]. 0.3 g of G/CNT powder prepared in 200 ml of distilled water and exposed to ultrasounds at 100 W for 2 hr. Then the amount of 20 g of AC powder is slowly added to the ultrasonic mixture for 3 hr. The mixture is then placed in the 50 °C for a day and then the water evaporates. The remaining solid layer was entering in tube quartz, under nitrogen atmosphere and slowly heated to 350 °C and remains for 2 hr. The residual product in reactor us AC/G/CNT composite. TEM image of the AC/G/ CNT composite structure was shown in Fig. (2).

2.3. Independent variables & experiment design

For economic removal of Mn^{2+} from the wastewater, it is necessary to find the optimum conditions of adsorption. Moreover, adsorption experimental parameters such as Mn^{2+} ions concentration (30130 mgL⁻¹), temperature (15-35°C), time (15-45 min), and pH (3.5-5.5) were studied in a batch mode. All experiments were conducted in 500 mL Erlenmeyer flasks. The levels of variables are shown in Table 1.

According to Table 1, for design of experiments because of various variables (each at 3 varied levels), Taguchi method was used. The software of Design Expert 8.3 was used to decrease the number of experiments to 9 based on Taguchi, and the results were shown in Table 2 include of detail of conditions.



Fig. 2. TEM image of AC/G/CNT composite (a) AC/CNT (b) G/CNT (c) AC/G.

	Independent Variables ^a				AC/G/CNT			AC
	Mn ⁺²	Temp.	Time		C ₀	C _e	Reduction	Reduction
No.	(mg/L^{-1})	(°C)	(min)	pН	(mg/L)	(mg/L^{-1})	(%)	(%)
1	0	-1	-1	0	80	4.26	94.68	88.02
2	0	0	0	+1	80	5.29	93.38	86.45
3	0	+1	+1	-1	80	7.07	91.16	84.81
4	-1	-1	+1	+1	30	1.15	96.18	89.38
5	-1	0	-1	-1	30	2.05	93.17	86.64
6	-1	+1	0	0	30	2.17	92.76	86.26
7	+1	-1	0	-1	130	13.20	89.85	84.49
8	+1	0	+1	0	130	13.85	89.35	83.15
9	+1	+1	-1	+1	130	17.90	86.23	80.31

Table 2. Condition of designed experiments by Taguchi method.

^a Batch Adsorption process

The surfaces of adsorbents are cleaned from pollutants, fats, and activates by alkali washing [8]. For this purpose, treatment of AC and AC/G/CNT hybrid as adsorbents were done before using by alkali washing. Therefore, adsorbents separately were poured into 5 wt.% of HCl, stirred for 25 min, and washed with hot distilled water. Then the adsorbents washed with 1 wt.% of NaOH solution to eliminate the residual HCl [9]. The samples were filtered and washed with pure water until the pH of the filtrating solution was neutral. Next adsorbents were dried in oven (OVEN, XU 112, France) at 90 °C for 6 hr. Ground and sifted to obtain fine powder. Finally, the adsorbents kept in desiccators for subsequent uses.

The required amount of adsorbents was introduced in a stirred tank reactor containing 250 mL of the prepared solution of Mn²⁺ ions. The flasks were mechanically agitating for the desired time, wished temperature in fixed 650 rpm. Solution of hydrochloric acid/sodium hydroxide 0.1 M was also prepared for pH adjustments. According to Table 2, after each condition, the adsorbent was separated from the solution and filtered (0.45µm cellulose acetate paper). All experiments were performed in duplicate. After filtration, Mn²⁺ ions remaining in the solution were determined with a Perkin-Elmer 3100 atomic absorption spectrophotometer. The amount of adsorbed Mn²⁺ ions was calculated using the $q_e = (C_0 - C_e) \times v/m$ equation. where qe is the quantity of adsorbed Mn²⁺ ions at equilibrium (mg/g), C_0 and C_e respectively are the initial and equilibrium concentrations of Mn²⁺ ions (mg/L),



Fig. 3. Effect of pH on adsorption.

V is the volume of metal solution (L), and m is the weight of adsorbent used (g). Moreover, the removal percentage of Mn^{2+} ions was calculated using the R(%) = $(C_0 - C_c)/C_0 \times 100$ equations.

3. Results and Discussion

3.1. Effect of pH

According to surface chemistry, the amount of Adsorption depends on the surface behavior of adsorbent, such as porosity and situation and distribution of active sites for bonding with metal ions. These indexes generally depend on the pH of the solution [10]. At this study the pH solution was varied at 3.5, 4.5 and 5.5. During adsorption process, pH of solution adjustment at fix purposed value and measure with a pH meter using a combination glass electrode. Figure 3 indicates the effect of pH solution on the removal of Mn²⁺ ions onto AC and AC/G/CNT composite from aqueous solutions at 30 min.

The Mn^{2+} removal was 86.45% and 93.38% at pH 3.5 by AC and AC/G/CNT respectively, it was 86.26% and 92.76% for adsorbent at pH which is equal to 4.5 and decreased 84.49% and 89.85% for pH=5.5. It is seen that removal of Mn²⁺ was strongly dependent on pH conditions at AC/G/CNT than AC as an adsorbent. In addition, the percentage removal of Mn²⁺ first sharply increased by increasing of the pH until 4.5 and half flat in higher pH of solution more than 4.5. Good adsorption at middle range of pH (4.5) indicates that low pH leads to an increase in H⁺ ions on the Adsorbents surface, resulting in significantly strong electrostatic attraction between positively charged surface of Adsorbents and Mn²⁺ ions. At higher pH values, from 4.5, the precipitation of Mn²⁺ ions is occurred and both ion exchange and aqueous metal hydroxide formation are then occured. So the best value of solution pH is equal to 4.5.

3.2. Effect of Time

Contact time is a significant factor affecting removal of initial Mn^{2+} ions in the solution. Effect of time on the adsorption was shown in Table 2. The Results reveal that increasing contact time caused

increasing the adsorption of Mn²⁺ ions or different initial concentrations. So, if the time increases from 15 to 30 min, the amount of absorption increases with more slopes, while with increasing time from 30 to 45 min, the absorption rate increases with less intensity. The Mn²⁺ removal is higher at the first 30 min. This is due to larger surface area of the Adsorbents at the beginning for the adsorption of Manganese. It has been matched with other results [11]. For example, at fix Mn²⁺ concentration 80 mg/l, with the increasing time from 15 to 30 min, the absorption rate was 3.6% while with the increasing time from 30 to 45 min, this value was changed by only 2%. Therefore, based on economic considerations and the rate of absorption changes, the best time for the absorption process is 30 min.

3.3. Effect of temperature and Mn^{2+} Concentration Thermodynamically behavior of large amount adsorption process is exothermic and so temperature has a negative effect on removing metal ions and other pollutants [12]. According to this, the mechanism of Mn²⁺ ions adsorption by AC and AC\G\CNT was a function of temperature and has been considered this research. Figure 4 shows the effect of temperature on Mn²⁺ removing for both adsorbents of AC and AC\G\CNT.

The results of figure 4 were shown at initial concentration of 30 mg Mn^{2+} removing decreased

from 89.3% to 84.1% by AC and 96.18% to 91.16% by AC\G\CNT with increasing of temperature from 15 to 35 °C. This change for high concentration of Mn²⁺ is more evident at higher temperatures. But the best initial concentration of Mn²⁺ is 80 mg/L⁻¹. At higher concentrations of this, between the adsorption of metal ions and the surface of adsorbent, a competition phenomenon was occurred based on steric hindrance and as a result, the amount of absorption decreases. The simultaneous effect of three variables include initial Mn²⁺ concentration in the range of 30, 80, and 130 mg/L for temperatures of 15, 25, and 35 °C and contact time of 15, 30, and 45 min were done at fixed pH of 4.5, and the results are shown in Figure 5.

Based on Figure 5, it is observed that the effect of Temperature on amount of absorption is more than time because by increasing temperature, this decreases with a constant trend. However, when time increases, the amount of adsorption decreases, and then it is flat that due to the saturation of the adsorbent surface. It is also observed that the best absorption conditions occur at lower temperatures for medium concentrations of Mn^{2+} at 30 min. At lower Manganese concentration, the percentage removal of Mn^{2+} ions is high and by increasing temperature the slop of adsorption decreases, this means is the ratio of Mn^{2+} ions removing more decrease in high temperature. Therefore,



Fig. 4. Temperature effect on Mn²⁺ removing for both adsorbents.



Fig. 5. simultaneous effect of three variables on Mn^{2+} removing.

the technique of diluting wastewater and cooling during the removing process can be used to absorb more metal Mn^{2+} ions.

4. Conclusions

Generally, at fix conditions, the presence of G/ CNT hybrid in the structure of AC 7.5% increases the amount of adsorption. Moreover, the most important reason being to improve surface properties and create more porosity in the AC structure. In addition, the inherent property of CNT in absorption of Mn²⁺ ions based on ionic bonding under a wide range of graphene sheets has enhanced the absorption performance of AC. The best absorption conditions occurred at a 15°C and a concentration of 30 mg Mn^{2+} at pH of about 4.5. Increasing pH of the solution caused to the partial hydrolysis of Mn²⁺, bringing the arrangement of complexes. The result of this present shown adsorption of Mn²⁺ was exothermic mechanism and the rate of removing was decrease by increasing temperature. This difference is a result of the enhanced escaping tendency of metal ions moving and species in higher temperatures. In addition, a solubility increase in Mn²⁺ ions in water at higher temperatures caused decreasing sorption on surface of adsorbents. Ultimately, because AC is a basic, available and inexpensive sorbent, the results of this study will be useful for the removal of Mn²⁺ from industrial effluents.

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