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Removal of Cadmium from Aqueous Solution with Carboxymethyl Cellulose Hydro-gel: Adsorption Conditions and Affecting Factor

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In this research paper, the possibility of using carboxymethyl cellulose (CMC) synthesized from cotton fibers for the removal of cadmium from aqueous solutions was investigated. The adsorption was found to depend on cadmium initial concentration, pH, CMC dosage, agitation rate and temperature of the experiments. The maximum removal was found to be 96 % for the cadmium concentration of 150 mg L^{-1} at 40 ºC and pH equal to 11 with 12 gL^{-1} of CMC by using agitation rate 120 rpm after 3 h. In addition, desorption of cadmium and recovery of it was 95 % at pH = 3. The studies showed that the CMC can be used as an efficient and cost-effective adsorbent material for cadmium removal from wastewater.

Key Words: Adsorption, Carboxymethyl cellulose, Removal, Cadmium.

INTRODUCTION

Heavy metal contamination from wastewater is a world-wide environmental concern. The removal of poisonous metals from wastewater is a topic of great interest in the field of water pollution[1]. Several metals such as chromium, mercury, lead, copper, cadmium, manganese, *etc.*, are known to be notably toxic[2]. Since 1990s, numerical calculations indicated that the worldwide cadmium discharge rate had reached 22,000 tons/year. Cadmium is commonly used in metallurgical alloying, ceramics, metal plating, photograph development, pigment factory, printing industries, alkaline batteries and electroplating. Cadmium, the metal considered in this study, is the broadly used materials and is not biodegradable[3], where an intake of excessively large amounts by people may lead to severe kidney failure, liver disease[2], emphysema, hypertension and chronic disorders, such as itai-itai disease[3,4].

Therefore, the maximum concentration limit for cadmium in drinking water has been strictly regulated. The world health organization (WHO) and the American water works association (AWWA) have recommended that the concentration of cadmium in drinking water[4] should not exceed 0.005 mgL^{-1}. The usual methods for removing heavy metals consist of precipitation, oxidation, adsorption, coagulation, evaporation, reverse osmosis, ion exchange, membrane filtration and extraction. Amongst these various water-treatment techniques described, adsorption has been the most broadly used because it is an economically feasible, flexible, availability of different adsorbents, easy handling and environmentally friendly method in practice[5,6]. Lately, there is growing interest in using low cost, non-conventional alternative materials and efficient as adsorbent. In this research a new material for adsorption of cadmium synthesized by using cotton fibers, which is considered as a kind of waste byproduct from the textile industry. The objective of this study is to investigate the adsorption capacity of CMC prepared by cotton fibers waste and its characteristics for the removal of cadmium[6]. The effects of various experimental parameters such as pH, the feed concentration, temperature, agitation rate and adsorbent dosage were studied[7].

EXPERIMENTAL

Production of carboxymethyl cellulose: Cotton short fibers that are pure cellulose as raw material were treated for 5 h with sodium hydroxide solution at concentration of 30 % (w/w). The pretreated alkaline cellulose was reacted with monochloroacetic acid (MCA) at concentration of 40 % (w/w). The mixture was stirred at 600 rpm on a magnetic hot-plate stirrer (VELP, Italy) at constant temperature of 75 ºC for 4 h. The CMC gel product was filtered from solvent. The product was purified with methanol[8] (Fluka, Germany), dried at 70 ºC in a conventional oven (Binder, Germany) for 1 h.

Scanning electron microscope (SEM) was used to take the fiber image of the synthesized CMC samples. The samples were freeze dried (EMITECH; Model IK750, Cambridge, UK) on a polished aluminum surface. After drying, the sample was sputtered with gold for 30s by Polaron machine (BAL-TEC, Model SCDOOS, Switzerland). Afterwards, SEM was performed with a Stereo scan (Phillips XL30, Holland) Microscope.

Analytical methods: For the removal of cadmium from wastewater by the produced CMC hydro-gel completely mixed batch reactor (CMBR) technique was used. In this study the cadmium solution was prepared artificially by various initial concentrations (50, 100 and 150 mgL^{-1}). The pH values of each solution used in these experiments were 3 to 11 in increments of 1.0 by adding 0.1 molL^{-1} HCl or NaOH solution. A 50 mL of solution was added to the beaker containing CMC with different dosage from 2 to 20 gL^{-1} mixed for 0.5 to 3 h by magnetic mixer with its rotating speed of 30 to 180 rpm. These experiments were carried out at temperature 20, 40 and 60 ºC. Then the hydro-gel adsorbent was separated from the solution using alcohol and then filtered. The remained cadmium concentration was analyzed by atomic adsorption method.

RESULTS AND DISCUSSION

The morphology of CMC was studied using scanning electron microscope. CMC has a fabric structure, therefore can be used as an absorbent for heavy metals like cadmium. Heavy metals can be trapped among CMC's fibers. In addition, due to cadmium has positive ion, it can be absorbed by negative ion in carboxyl group on CMC. The results indicate that the removal of cadmium from the solution is dependent on the ability of surface adsorption.

Effect of pH: The effect of various pH in the removal of cadmium is shown in Fig. 1. As data shown in this Figure, the removal of cadmium is strongly related to pH value of the solution. It is clear that the adsorption of cadmium is higher in alkaline pH range 6.5-11.0. However, the removal is small in acidic range and reaches a maximum at around pH 11. In the low pH value there is an opportunity for dissolution of the adsorbent and a consequent diminish in the active sites. In addition to this effect, the adsorbent surface plays as positive ion in acidic solution which is not favourable for cadmium adsorption. Because of these mentioned reasons, desorption and recovery of adsorbed cadmium carried out using decline in the pH value. In order to make the process of adsorption and recovery of cadmium more economical, it is necessary to regenerate the spent adsorbent. As shown in Table-1 the maximum percentage recovery of cadmium was 95 % with 0.1 M HCl solution. It is remarkable to make a note of that adsorption remains maximum 93 % up to the 3rd regeneration cycle and then goes down to 90 % in the 4th cycle. This behaviour signifies that the adsorbent can be used successfully four times after regeneration for the removal and recovery of cadmium from wastewater[9].

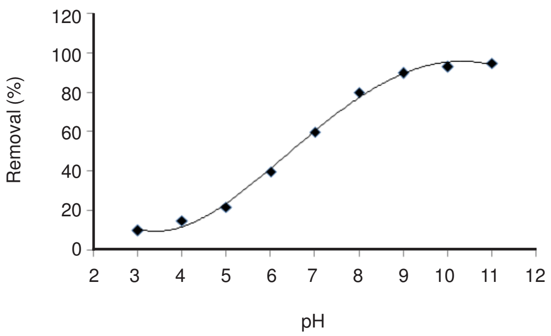

Fig. 1. Variation of cadmium removal percentage with various initial solution pH. (conditions: initial cadmium concentration 100 mg L^{-1}, temperature 40 ºC, adsorbent dosage 15 gL^{-1}, agitation rate 120 rpm and duration 150 min)

TABLE-1
EFFECT OF RECOVERY ON THE ADSORPTION AND DESORPTION OF CADMIUM BY CMC

Number of cycle	1	2	3	4
Cadmium (mgL^{-1}) before adsorption	20	20	20	20
Cadmium (mgL^{-1}) after adsorption	0.8	1	1.4	1.8
Removal (%)	96	95	93	91
Amount cadmium desorbed with 0.1 M HCl (mgL^{-1})	18.2	18	17.3	16.4
Recovery (%)	95	95	93	90

Effect of agitation time and initial concentration: It is clear from the Fig. 2 that the uptake of cadmium enhances with the lapse of time and achieves equilibrium in 150 min at an agitation rate of 120 rpm, temperature 40 ºC and pH equal to 10 for each concentration. These curves are showing the independent character of equilibrium period for the solute concentration. However, the adsorption of cadmium from wastewater by CMC increases with the initial concentration of cadmium. The increase in initial metal ion concentration decreased the per cent adsorption and increased the amount of metal uptake per unit weight of the adsorbent (mg g^{-1}).

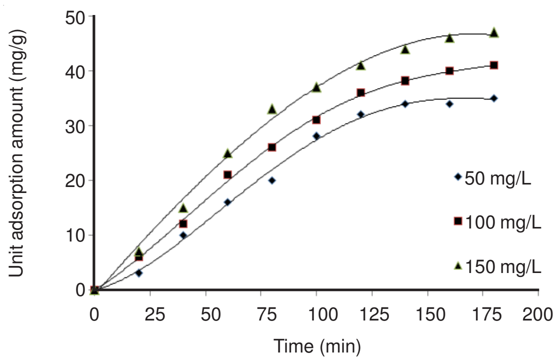

Fig. 2. Unit adsorption amount of cadmium by CMC at varied initial concentration and detention time, temperature: 40 ºC, agitation rate: 120 rpm and pH: 10

Effect of temperature: The temperature range used in this study was from 20 to 60 ºC. Adsorption enhanced with increasing in temperature to 40 ºC. This result (Fig. 3) suggests the endothermic nature of adsorption for this temperature range. Enhancement of adsorption capacity of CMC at 40 ºC may be attributed to the extension of adsorbent fibers and or activation of its surface[10]. The removal percentage of cadmium from the solution decreased from 95 to 90 per cent on increasing the temperature from 40 to 60 ºC at a pH of 10 and agitation rate of 120 rpm. This indicates the exothermic nature of the process in this limit, which may be due to a relative increase in the escaping tendency of the solute from the solid phase to the bulk phase with the rise in temperature of the solution[11].

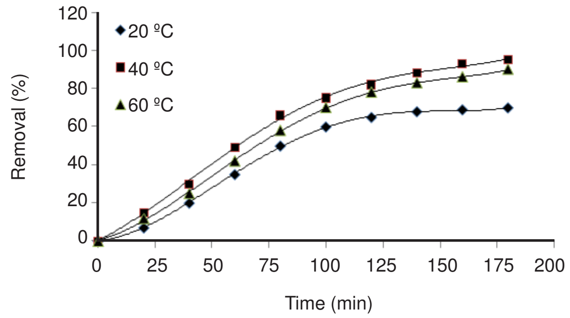

Fig. 3. Removal percentage of cadmium by CMC at varied temperature, agitation rate: 120 rpm, initial concentration: 150 mg L^{-1} and pH: 10

Effect of agitation rate: Fig. 4 shows the experimental results obtained from a series of initial concentration studies for cadmium removal in duration 150 min, 10 pH and 40 °C temperature. The rate of agitation was varied from 30 to 180 rpm. These results indicate that the unit adsorption amount of cadmium increases from 17 to 47 mgg^{-1} with the increase in the rotational speed from 30 to 120 rpm for 150 mgL^{-1} initial concentration of cadmium. This may be explained by the fact that the rising agitation rate diminishes the boundary layer resistance to mass transfer in the bulk and increases the driving force of cadmium ions[11]. On the other hand, the unit adsorption amount of cadmium decreases with increase in agitation rate from 120 to 180 rpm. It may possibly be attributed to mix excessively which it causes the cadmium ions return to bulk phase.

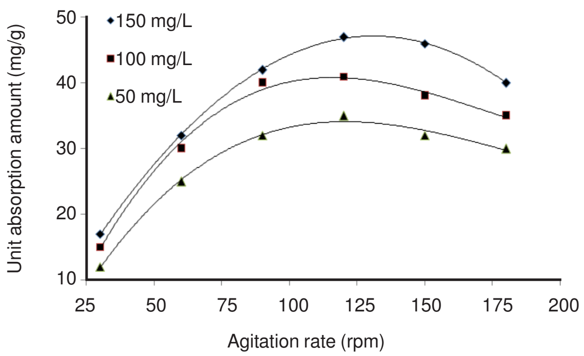

Fig. 4. Unit adsorption amount of cadmium by CMC at varied initial concentration and agitation rate, temperature: 40 ºC, duration: 150 min and pH: 10

Effect of adsorbent dosage: In order to investigate the effect of adsorbent dosage, the dosages of CMC in the aqueous solution were 2 to 20 g L^{-1} that increases 2 g L^{-1} in each sample. These experiments were carried out at 40 ºC, agitation rate 120 rpm, initial concentration of cadmium 150 mg L^{-1}, pH adjust to 10 and duration 150 min. The effect of adsorbent dosage is shown in Fig. 5. Based on these results, the cadmium removal efficiencies of the CMC adsorbent were calculated (Fig. 5). It is apparent that, although the amounts of cadmium removed increased with increasing dosage, the unit adsorption amount decreased continually from 47 to 3 mg g^{-1}. This trend was very sharp when the adsorbent dosage was in the range of 2 to 12 g L^{-1} and afterward gradually leveled at higher dosage (dosage >12 g L^{-1}). The total removal per cent and the unit adsorption amount of the adsorbent appeared to change with dosage in a different manner. Thus, there is a requirement for finding an optimum adsorbent dosage to satisfy both the total cadmium removal and the adsorption efficiency. Based on the mentioned trends the optimum adsorbent dosage was determined to be 12 g L^{-1}.

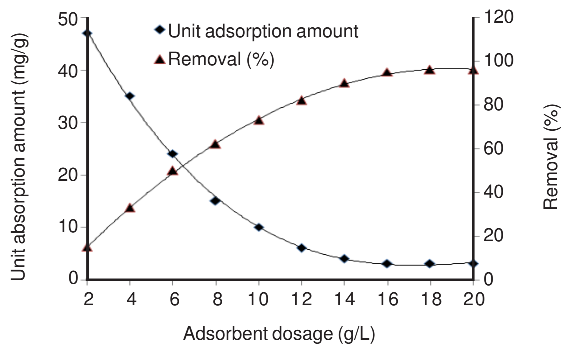

Fig. 5. Unit adsorption amount and removal percentage of cadmium by CMC at varied adsorbent dosage, temperature: 40 ºC, duration: 150 min, agitation rate: 120 rpm and pH: 10

Conclusion

The removal of cadmium from aqueous solutions seems possible by adsorption onto CMC synthesized using cotton fibers. The different factors studied have a great effect on the amount of removal and the maximum removal 96 % has been achieved at optimum conditions that are cadmium initial concentration 150 mgL^{-1}, pH 11, retention time 150 min at 120 rpm agitation rate with 12 gL^{-1} of CMC. Also, the desorption of cadmium for recovery of adsorbent was achieved 95 % at pH = 3. Base on these results, it is possible to reuse the adsorbent for reducing the operation costs.

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