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Using Modified Sawdust for Removal of Chromium (VI) from Aqueous Solutions

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ABSTRACT: Chromium is abundant in nature and has a dominant presence in most of the effluent streams as compared to other heavy metal ions. The presence of highly toxic and carcinogenic Cr(VI) in effluent streams is a major environmental issue. The electroplating and tannery industry effluents are the major source for the Cr (VI) production in wastewater streams. In this study sawdust modified by diethylenetriamine and used as an adsorbent .The effects of various parameters such as solution pH (pH=3), adsorbent dosage (2 g/L), contact time(30 min), agitation rate(100 rpm) and initial Cr (VI) concentration on the removal of Cr (VI) have been studied. The Langmuir and Freundlich isotherms were applied to the adsorption process and their constants were evaluated. The Freundlich model was found to be most appropriate for the description of the adsorption process.

Keyword: Modified sawdust, chromium (VI), diethylenetriamine, Isotherm and Removal.

INTRODUCTION

In recent decades, the pollution of water resources has been one of the major concerns of human, so several studies have been carried out for the purpose of removing pollutions from water. The heavy metal pollution is of greatest concern among the kinds of environmental pollution because of heavy metals is high toxicity and mobility. Adsorption of heavy metals from aqueous solution is an efficient technology in industrial wastewater treatment (elhami *et al*., 2013). The choice of appropriate sorbent for adsorption is a critical parameter in order to obtain fast, efficient and high removal. For this reason introducing new sorbent is a still challenge. Recently, there has been an increasing emphasis on the adsorbents with low cost for pollution removal. Natural materials that are available in large quantities from agricultural operations may have the potential to be used as low cost sorbents; because they are widely available and environmentally friendly (Anwar *et al*., 2010). Sawdust is a low cost material that has been used as adsorbent (Yasemin and Zeki, 2007; Laasri *et al*., 2007). However, its adsorption capacity is low for some compounds. Chemically modified sawdust has been identified as an innovative and promising class of adsorbent materials. Different adsorbents have used to the removal of chromium (VI) from water samples such as *Ocimum americanum* L. seed pods (Lena Kumar *et al*., 2008), *Helianthus annuus* (sunflower) stem waste (Jain *et al*., 2009), *Eucalyptus* (Vikrant and Pant, 2006), neem sawdust (Vinodhini and Das, 2009), sawdust (Vinodhini and Das, 2010), aniline formaldehyde condensate coated silica gel (Albino Kumar *et al*., 2007), montmorillonite-supported magnetite nanoparticles (Yuan *et al*., 2009), modified Ca-montmorillonite with ionic liquids (Li *et al*., 2014), green alga *Ulva lactuca* and its activated carbon (El-Sikaily *et al*., 2007) and UAE sand (Khamis *et al*., 2009).

This study reports the efficiency method for the adsorption of chromium (VI). Sawdust was modified by diethylenetriamine (DETA). Modified sawdust has a higher surface area than sawdust and adequate sites for adsorption (amine groups) of chromium (VI) (Elhami *et al*., 2013). The effects of pH value of the solution, adsorbent dose, adsorption time and the initial concentration on the adsorption of chromium (VI) on modified sawdust have been investigated.

MATERIAL AND METHODS

A. Material

All reagents were analytical grade and were used without further purification. A 1000 $\mu g mL^{-1}$ stock solution of chromium (VI) was prepared by dissolving 1.415 g of potassium dichromate (Merck, Germany) in 100 mL water. Working solutions were freshly prepared by appropriate dilution of the stock solution with water.

B. Preparation of adsorbent

The sawdust supplied by a local wood processing factory was washed with distilled water to remove impurity, and then dried overnight at 60ºC. The dried sawdust was sieved to retain the 0.5 mm fractions for further chemical synthesis. 140 mL of HCl concentrated (Merck, Germany) was added to 10 g of sawdust.

After allowing it to stand for 2 h, 60 mL of diethylenetriamine (Merck, Germany) was added too. After allowing it to stand for 30 min, the product was filtered, washed with distilled water, and dried in oven at 40ºC for 24 h.

C. General procedure

All the experiments were carried out in batch mode. Batch mode was selected because of its relative simplicity. The experiments were run in Erlenmeyer flasks (100 mL) using shaker. Prior to each experiment, predetermined amount of adsorbent was added to each flask with 50 mL of aqueous chromium (VI) solution. The desired pH was maintained using dilute NaOH or HCl solutions. All the adsorption experiments were carried out at room temperature (25 ± 2°C) and a pH of 3, unless stated otherwise. The shaking was kept constant for each run throughout the experiment ensuring equal mixing. Samples of 10 mL were taken, centrifuged and analyzed for chromium (VI) concentration measurements. The concentration of chromium (VI) ions was determined spectrophotometrically by developing a purple-violet color with 1, 5-diphenyl carbazide in acidic solution as complexing agent. The absorbance of the purple-violet colored solution is read at 542 nm.

The percentages of chromium (VI) removal are calculated based on the following equation:

$$Removal(\%) = (\frac{C_{0-}C_e}{C_0}) \times 100 \quad (1)$$

In this equation, C_0 is the initial chromium (VI) concentration (before being mixed with the adsorbent), and C_e is the equilibrium concentration (after being mixed with the adsorbent). The equilibrium concentration was obtained through a calibration curve for the chromium.

RESULTS AND DISCUSSION

Modified sawdust by diethylenetriamine was chosen as an adsorbent for removal of chromium (VI) from water samples. The preliminary experimental observations showed that modified sawdust removed chromium (VI) from water more than 81%, while sawdust did not have this ability (only about 40 %).

A. The effect of pH

The adsorption of chromium (VI) onto the adsorbent as a function of pH was investigated at the initial concentration of 20 mg/L and the contact time of 30 min. The removal of chromium (VI) was maximum in the pH of 3.0 (Fig. 1) so pH=3.0 was chosen as optimum.

B. Effect of adsorbent dose

The influence of adsorbent dose on chromium removal was studied by varying the adsorbent dose from 1.0 to 8.0 g L^{-1} at an initial chromium concentration of 20 mg/L in 50 mL solutions. Increased adsorbent dosage implied a greater surface area and a greater number of binding sites available for the constant amount of chromium (VI). An adsorbent dose of 2 g/L was chosen as an optimum value (Fig. 2).

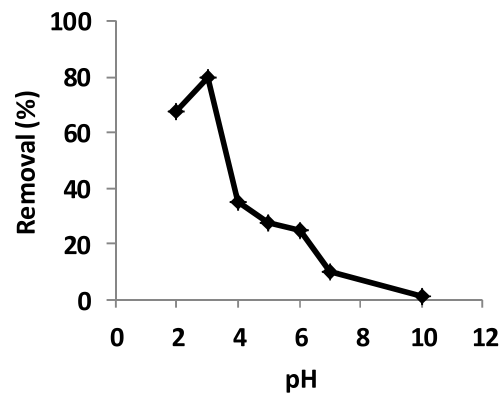

Fig. 1. Effect of pH on Cr (VI) removal.(initial Cr(VI) concentration 20 mg/L, adsorbent dosage=2 g/L, contact time=60 min, agitation rate= 120 rpm).

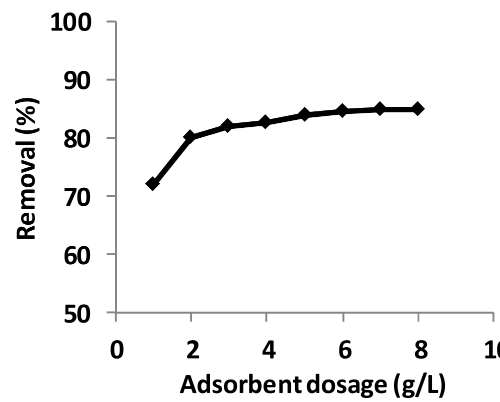

Fig. 2. Effect of contact time on adsorption of Cr(VI). (initial Cr(VI) concentration 20 mg/L, pH=3.0, contact time=30 min, agitation rate= 120 rpm).

C. Effect of contact time and Agitation Rate

The adsorption of chromium(VI) onto modified sawdust has been investigated as a function of time in the range of 2-90 min, as it is demonstrated in Fig. 3. In each adsorption experiment, 50 mL of dye solution of known concentration and pH was added to 0.1 g of the adsorbent in 50 mL round bottom flask at room temperature and the mixture was stirred on a shaker at 120 rpm. As the results indicated, removal of chromium(VI) using the adsorbent occurred quickly and it was not a highly time-dependent process. by modified sawdust. The agitation speed was also surveyed ranging between 60 to 200 rpm. During all agitation speeds the removal was not varied significantly (Fig. 4).

It was found that about 75% removal of chromium (VI) occurs within 5 min. However, for a removal of more than 80%, a time interval of 30 minutes was needed. This confirms a high and rapid adsorption of chromium (VI) An agitation speed of 100 rpm was chosen as an optimum value. The small effect of agitation showed that external mass transfer was not the rate limiting step.

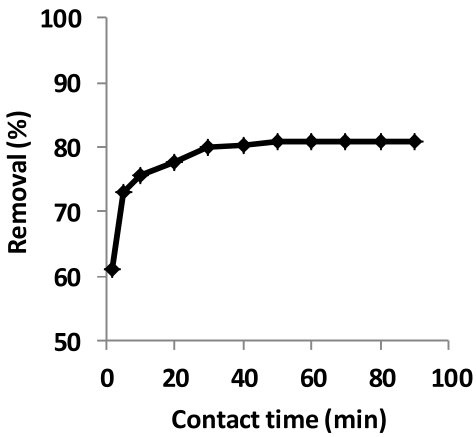

Fig. 3. Effect of contact time on adsorption of Cr (VI) (initial Cr(VI) concentration 20 mg/L, adsorbent dosage=2 g/L, pH=3.0, agitation rate= 120 rpm).

D. Initial concentration

In all the cases of optimization, the concentration of chromium (VI) was 20 mg/L. In order to study the possibility of chromium (VI) removal in other concentrations with the same optimization condition, other concentrations were studied as well. The results showed that the optimization condition was applicable for concentrations from 5 to 70 mg/L with chromium (VI) removal being 70-95% (Table 1).

E. Interference studies

In order to evaluate the selectivity of the method, the effects of different ions on the adsorption of chromium (VI) were investigated.

A constant concentration of chromium (VI) (20 mg mL^{-1}) was taken with different concentrations of ions and the general procedure was followed. Any deviation of ±5 % or more from the absorbance value of the standard solution was considered as interference. Results given in Table 2 indicate that the proposed method is relatively selective for the determination of chromium (VI).

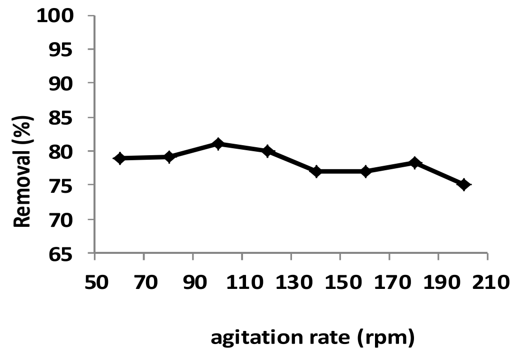

Fig. 4. Effect of agitation rate on adsorption of Cr (VI). (initial Cr(VI) concentration 20 mg/L, adsorbent dosage=2 g/L, pH=3.0)

Table 1: Removal for deferent initial concentrations of Cr (VI).

Concentration of Cr (VI) (mg/L)	Removal of Cr (VI) (%)
5	94/2
10	93/1
20	81/0
30	78/6
40	78/0
50	75/2
60	72/3
70	71/7
80	70/8

F. Isotherms of Adsorption

In this study, Langmuir and Freundlich isotherms were employed for the study of the adsorption of chromium (VI) onto modified sawdust. Such isotherms were achieved for an initial concentration of 5-80 mg/L in the previous optimization condition, contact time =120 min and a temperature of 25±2°C; and q_e is achieved through following equation:

$$q_e = (C_0 - C_e)\frac{V}{W} \quad (2)$$

Table 2: Effect of the interference of diverse ions on the removal of Cr (VI).

Diverse ion	Concentration of ions (mg/L)
Na^+, Ca^{+2}, Ag^+, Cu^{+2}, Mg^{+2}, Ba^{+2}, K^+, Zn^{+2}	15
Cd^{+2}	20
NO_3^-, Br^-, HPO_4^{-2}, Cl^-	25

In this equation, q_e is the adsorption capacity in an equilibrium of (mg/L); C_0 is the initial concentration of chromium (VI) (mg/L); C_e is the equilibrium concentration (mg/L); *V* is the volume of solution; and W is the weight of the adsorbent.

In order to study the adsorption of chromium according to Langmuir Isotherm the following equation (2) was used, in which q_m and K_a are the constants of Langmuir (Langmuir, 1916). A plot of $1/q_e$ versus $1/C_e$ gives KQ and q_m if the isotherm follows the Langmuir equation. The results were presented in Table 3.

$$\frac{1}{q_e} = (\frac{1}{K_a q_m})(\frac{1}{C_e}) + \frac{1}{q_m} \quad (3)$$

The Freundlich model assumes a heterogeneous adsorption surface with sites that have different adsorption energies which are not equally available (Freundlich, 1906). This isotherm is achieved through equation (3), in which K_f is the constant of Freundlich and is dependent on the adsorption capacity by the adsorbent. For this isotherm, log q_e was plotted versus log C_e. The results were presented in Table 3.

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (4)$$

G. Adsorption kinetic studies

The adsorption was considered as the pseudo-first order and pseudo-second-order kinetic models (Lagergren,. 1898; Ho and Mckay,. 1999). Parameters for pseudo-first and pseudo-second order models from liner regression for concentrations of 10 and 20 (mg/L) of chromium (VI) are summarized in Table 4. According to Table 4, the adsorption kinetics well fitted using a pseudo second-order kinetic model.

Table 3: Langmuire and Freundlich isotherms parameters for the removal of Cr(VI).

Langmuire isotherm parameters			**Freundlich isotherm parameters**	
q_m(mg/L)	K_1	R_L	K_f (mg/g)	n
15.11	1.83	0.03	6.77	2.30

Table 4: Kinetic parameters for the removal of Cr(VI).

Pseudo First order				
Concentration (mg/L)	**q_e, exp (mg/g)**	**q_e (mg/g)**	**K_1 (min^{-1})**	**R^2**
10	4.74	0.35	0.05	0.9545
20	8.17	1.78	0.09	0.9589
Pseudo- second -order				
Concentration (mg/L)	**q_e, exp (mg/g)**	**q_e (mg/g)**	**K_2 (min^{-1})**	**R^2**
10	4.74	4.70	0.96	0.9999
20	8.17	8.20	0.16	0.9998

H. Real Samples Study

The researchers studied chromium (VI) removal from real samples of the waters from Ahvaz city water, rivers water and the industrial wastewaters. To do this, 25 mL of each real sample was examined, different amounts of chromium (VI) were added to them and the removal process was studied on them. The results showed that the method is suitable for the analysis of real samples.

CONCLUSION

The present investigation evaluated the fact that the chemically modified sawdust by diethylenetriamine is effective adsorbent for the removal of chromium (VI) from different water samples. The effects of these parameters on the adsorption of Cr (VI) were examined applying optimal experimental conditions. The results showed that 1 g/L of modified sawdust is required for the removal about 70% of chromium (VI) from initial concentrations of 20 mg/L. However, for a removal of more than 75%, 2 g/L of adsorbent was needed at only 5 min. The results are better than some of the previously reported methods (Lenakumar *et al*., 2008; Jain *et al*., 2009; Albino Kumar *et al*., 2007). From the experimental results, it was found out that for Cr (VI) concentrations ranging 5-70 mg/L, quantitative removal was obtained in a single adsorption. The method was applied for the removal of chromium (VI) from real samples of different waters such as industrial water, river water and tap water samples, the results showed that the method is suitable for the analysis of real samples. A high removal, simplicity and high adsorption capacity of adsorbent are the main advantages in this method.

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