REMOVAL OF CHROMIUM(VI) FROM AQUEOUS SOLUTIONS USING SAWDUST AS ADSORBENT

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ABSTRACT :

In the present study, a low cost adsorbent is developed from the naturally available sawdust which is biodegradable. The removal capacity of chromium(VI) from the synthetically prepared industrial effluent of electroplating and tannery industrial is obtained.

Two modes of operation are used, batch mode and fixed bed mode. In batch experiment the effect of Sawdust dose (4- 24g/L) with constant initial chromium(VI) concentration of 50 mg/L and constant particle size less than1.8 mm were studied.

Batch kinetics experiments showed that the adsorption rate of chromium(VI) ion by Sawdust was rapid and reached equilibrium within 120 min. The three models (Freundlich, Langmuir and Freundlich-Langmuir) were fitted to experimental data and the goodness of their fit for adsorption was compared. In the fixed bed isothermal adsorption column, the effect of particle size (dp) (1.09-1.8) mm, influent flow rate (Q) (1- 4) L/hr, bed depth (H) (25- 35) cm and the pH(1-7)of the solution were studied .The results show that Sawdust is an efficient adsorbent for the removal of Cr(VI) from wastewater. Percent removal of chromium reaches (100%) with increasing of contact time and decreasing the pH.UV- Spectrophotometer was used to determine the metal ion concentration.

ازالة الكروم من المياه الملوثة باستخدام نشارة الخشب كمادة مازة

الخلاصة :

امكانية استخدام المواد الفائضة والرخيصة الثمن مثل نشارة الخشب المطروحة من ورش النجارة كمواد مازة لبعض الايونات المعدنية الموجودة في المياه الملوثة مثل ايونات الكروم (VI) تمت دراستها.

تم استخدام نمطين من التشغيل في هذا البحث وهي تجارب النمط الدفعي (batch experiments) وتجارب النمط المستمر (fixed bed experiments). تم اجراء تجارب دفعية (batch experiments) لدراسة تأثير كمية نشارة الخشب (24-4)غم/ لتر بثبوت التركيز الابتدائي لايون الكروم(50 ملغم/ لتر) وحجم ثابت لجزيئات المادة الممتزة الذي هو اقل من 1.8 mm أظهرت النتائج ان نسبة ازالة المعدن تزداد بزيادة كمية نشارة الخشب و الزمن. كذلك أظهرت النتائج ان الوصول الى حالة التعادل تستتغرق تقريباً (120)دقيقة، تم تحليل النتائج باستخدام موديلات (Langmuir, Freundlich and Langmuir-Freundlich) وأظهرت النتائج ان جميع الموديلات ذات تقارب جيد. كذلك اجريت تجارب النمط المستمر (fixed bed experiments) وتم دراسة حجم جزيئات المادة الممتزة (1.09 -1.8) بمعدل جريان داخل (1-4) لتر/ ساعة وارتفاع عمود الامتزاز (25-35) سنتمتر وحامضية المحلول (1-7). لقد أظهرت النتائج نشارة الخشب هي فعالة في امتزاز المعادن من مياه الصرف وكانت اعلى نسبة ازالة الكروم تصل (100%) بزيادة زمن العملية والمساحة السطحية وفعالية المادة الممتزة .

KEY WORDS :

Wastewater, Adsorption, Chromium(VI), Heavy metals removal, Sawdust, Low cost adsorbent.

INTRODUCTION :

Environmental contamination by toxic metal is of great concern because of health risks on humans and animals.Among the toxic metal ions , chromium is one of common contaminants which gains importance due to its high toxic nature even at very low concentrations(Vinodhini and Das, 2010).

Chromium(VI) is a cancer-causing agent and can pose health risk such as liver damage (Dokken et al.,1999).

Waste waters such as those generated during dyes and pigments production ,film and photography,galvanometry,metal cleaning, plating and electroplating may contain undesirable amounts of chromium(VI) anions(Venkateswaran ,2007 ;Bhattacharya ,2008).

Concentration of Cr(VI) present in industrial effluent streams are in the range of 50-200 mg/l(Contreras ,2004 ; Kumar and Bishnoi,2007).The permissible limit of Cr(VI) in potable water is 0.05 mg/l(Selvaraj and Manonmani ,2003).

In order to comply with the permissible limit,it is essential that industries treat their effluents to reduce the Cr(VI) concentration in water and wastewater to the acceptable level before its disposal or recycling into the natural environment.

There are various treatment technologies available to remove Cr(VI) from waste water such as chemical precipitation (Uysal and Irfan ,2007)Ion-exchange(Uysal and Irfan ,2000) , membrane separation(Kozloovski and Walkowiak, 2002),electrocoagulation(Roundhill and Koch ,2002),solvent extraction(Chen ,2004),reduction(Chen and Hao ,1998)reverse osmosis, and adsorption(Baral et al. , 2007 ; Mohan et al. , 2005). These techniques are economically expensive for the removal of Cr(VI) from wastewater.The above mentioned removal techniques have many disadvantages such as incomplete metal removal,high reagent and energy requirements, and generation of toxic sluge or waste products which require proper disposal without creating any problem to the invironment(Aliadadi et al. , 2006). Therefores , there is a dire need of a treatment method for Cr(VI) removal from wastewater which is simple,effective and inexpensive(Babu and Gupta , 2008).Adsorption when combined with an appropriate step of desorbing the Cr(VI) from adsorbent and avoiding the problem of disposal of adsorbent is a cost effective and versatile method for the removal of Cr(VI) (Kumar et al. , 2007).

The cost associated with commercial adsorbents make adsorption process very expensive which has led to the search for new stratgies for developing low-cost materials with a good capacity for Cr(VI) removal(Aggarwal et al. , 1999).In the recent years ,several studies have been reported on various low-cost adsorbents such as wool(Dakiky et al. ,2002) used tyers, seaweed, fungal biomass, green algae, maple sawdust(Shukla et al. , 2003),sugar industry waste,rad mud,tea factory waste(Malkoc and Nuhoglu,2005).

However,many of these naturally available adsorbents have low chromium adsorption capacity. Thus, there is a need to develop or find innovative low-cost adsorbents with an affinity towards metal ions for the removal of Cr(VI) from aqueous solution which leads to high adsorption capacity(Kumar and Bishnoi ,2008).

The objective of the present study is to investigate the possible use of sawdust as alternate adsorbent material for the removal of Cr(VI) from wastewater. Continuous adsorption experiments were conducted to understand and quantify the effect of influencing parameters such as flowrate, bed depth, partical size, pH of the solution.

Batch experiments are carried out for kinetic studies on the removal of Cr(VI) from aqueous solution. The Langmuir,Freundlich, Langmuir-Freundlich,equation models are used to fit the experimental equilibrium isotherm data obtained in this study.

EXPERIMENTAL WORK

Materials :

Adsorbent: Sawdust is collected from the Iraqi workshops.It is washed repeatedly with distilled water to remove the dust and soluble impurities.It is then kept for drying at room temperature for 8 hr.

The sawdust were sieving to produce a particle size(1.09,1.59,1.8mm).

Adsorbate : A stock solution of 1000mg/l of Cr(VI) is prepared by dissolving 2.828 gm of 99.9% Potassium dichromate(K_2 Cr_2 O_7) in 1000 ml of solution .This solution is diluted as required to obtain the standard solutions containing 10-100mg/l of Cr(VI),pH adjustment is carried out by using 0.5N HCl and 0.05N NaOH solutions.

EXPERIMENTAL MODES :

1) Batch Experiments

Batch experiments were used to obtain the equilibrium isotherm curves and then the equilibrium data. In batch mode effect of sawdust dose on adsorption process and equilibrium isotherm experiments were studies.

All experiments were carried out at 25C^o ±1 ,rpm=120 and pH=1 . Five of 1 liter flasks were used for all experiments conducted with an initial chromium (VI) concentration of 50 mg/L, sawdust dose was of (4,8,12,16,20,24) g/L. Samples were collected from the flasks and tested using (Shimadiza UV – 160) by determining the absorbance of the chromium ions with 1cm cell width (1cm layer thickness).

Data obtained from batch tests fitted to Freundlich, Langmuir and Freundlich-Langmuir adsorption isotherm equations.

2) Fixed Bed Column Experiments

Column experiments were carried out at various particle size (dp), flow rate (Q), bed depth (H), pH of the solution , to measure the breakthrough curves for the systems.

The fixed bed adsorber studies were carried out in Q.V.F. glass column of 3.5 in. (8.75cm) I.D. and 50 cm in height. The sawdust was confined in the column by fine mesh at the bottom to avoid loss the adsorbent. The influent solution was introduced to the column through a small water distributor and class balls to ensure a uniform distribution of influent through the adsorbent, fixed at the top of the column.

The experimental procedure as follow: The sawdust was placed in the adsorption column for the desired bed length and particle size.

- The wastewater with the desired concentration was prepared in the feed container, using distilled water.
- The wastewater was pumped to the adsorption column through the calibrated rotameter at the desired flow rate.
- Samples were taken periodically for concentration of metal measurment using UV-Spectrophotometer.
- The breakthrough curves were determined by plotting relating effluent concentration (C/Co) against time (t).

The schematic representation of experimental equipment is shown in **Fig 1**.

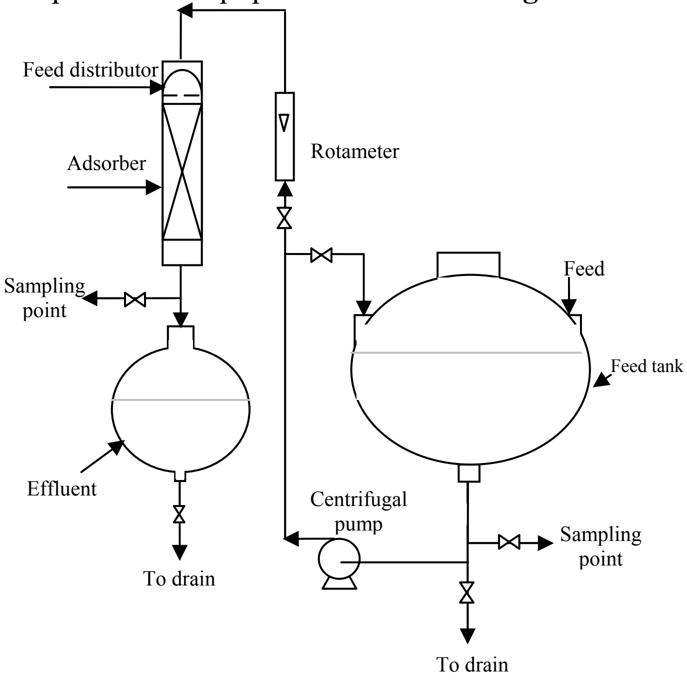

Fig. (1) Schematic representation of fixed bed experimental

RESULTS AND DISCUSSION:

Batch Experiments:

(i) Adsorption Isotherms:

Adsorption isotherm studies were performed to obtain equilibrium isotherm curves and data required for the design and operation of fixed bed adsorber. The adsorption isotherm curves were obtained by plotting the weight of the solute adsorbed per unit weight of the adsorbent (q_e) against the equilibrium concentration of the solute (c_e). **Fig. 2** shows the adsorption isotherm curve for adsorption of Cr(VI) on sawdust at 25 C^o .

The obtained data was correlated with Langmuir, Freundlich and Langmuir-Freundlich models. The Langmuir model describing adsorption can be described in **eq. (1)**as (Weber and Walter , 1972):

$$\frac{x}{m}=\frac{abC_e}{1+aC_e} \tag{1}$$

The Freundlich adsorption model in **eq. (2)** of the form (Weber and Walter, 1972):

$$\frac{x}{m}=kC_e^{1/n} \tag{2}$$

Combination of Langmuir-Freundlich Isotherm Model, i.e. the Sips model for single component adsorption (Sips, 1984)as in **eq.(3)**:

$$q_e=\frac{bq_mC_e^{1/n}}{1+bC_e^{1/n}} \tag{3}$$

The parameters for each model obtained from non-linear statistical fit of the equation to the experimental data. All parameters with their correlation coefficients are summarized in **Table 1**.

From the statistical analysis (high values of the correlation coefficients) it was found that adsorption of metal by sawdust could be well described by the three isotherm models. The correlation coefficients were in the range of (0.956-0.9591 %) for initial chromium concentration 50 mg/l.

The correlation coefficient value was higher for Freundlich than the other correlations. This indicates that the Freundlich isotherm is clearly the better fitting isotherm to the experimental data.

Table 1 : Isotherm parameters for chromium(VI) Adsorption onto sawdust with the Correlation Coefficient.

Chromium solution		
Model	**Parameters**	**Values**
Langmuir eq.(1)	a,	0.006961
	b,	33.76436
	Correlation coefficient (R^2)	0.956
Freundlich eq.(2)	K,	0.279032
	n,	1.113541
	Correlation coefficient (R^2)	0.959166
Combination of Langmuir-Freundlich eq.(3)	q_m,	110.5533
	b,	0.002475
	n,	2.1842
	Correlation coefficient (R^2)	0.95851

FIXED BED EXPERIMENTS:

(i) Effect of Volumetric Flow Rate:

In a design of fixed bed adsorption column, the contact time is the most significant variable and therefore the bed depth and the metal solution flow rate are the major design parameters . The effect of varying the volumetric flow rate was investigated at constant concentration (50 ppm) and constant particle size (1.59) mm and bed depth (30) cm and solution pH(2), the breakthrough curves are presented in **Fig.5**. It is obvious that increasing the flow rate decreases the volume treated until breakthrough. This is due to the decreased contact time between the metal and the adsorbent at higher flow rate.

Increasing the flow rate may be expected to make reduction of the surface film. Therefore, this will decrease the resistance to mass transfer and increase the mass transfer rate. Also, because the reduction in the surface film is due to the disturbance created when the film of the bed increased resulting of easy passage of the adsorbate molecules through the particles and entering easily to the pores, this decreased contact time between metal and sawdust at high flow rate. These results agree with that obtained by(Kim et al. 2003) .

(ii) Effect of Bed Depth:

The effect of bed depth was investigated for metal adsorption on sawdust; the experimental breakthrough curves are presented in **Fig. 6.** The breakthrough curve was obtained for different bed depth of sawdustat constant flow rate (2 l/h),pH(2), constant particle size (1.59) mm and constant chromium(VI) concentration (50 ppm). **Fig.7** shows the effect of using bed depth of 60 cm. at pH=7, flow rate(2l/h) , and particle size (1.59) mm on breakthrough curve,it was clear that increasing the bed depth causes to increase the metal removal and can reach that obtain with pH=2 and bed depth of (30)cm at flow rate(2l/h), and particle size (1.59) mm. The increase in bed depth increases the breakthrough time and the residence time of the solute in the column, due to provide greater surface area(Malkoc and Nuhoglu,2006).

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(iii) Effect of Particle Size:

In case of using an adsorbent particles of much smaller size to an extent, that will eliminate inter particle mass transfer resistance, so that the rate determining step is diffusion through film around each particle. The effect of varying the particle size was investigated; the experimental breakthrough curves are presented in **fig.8 t**he breakthrough curves were obtained for different particle size (1.8,1.59,1.09) mm at constant initial concentration of chromium(VI)(50ppm),bed depth of Sawdust (30 cm) ,pH (2) and constant flow rate(2l/h).The experimental results showed that fine particle size (1.09mm) showed a higher metal removal than others particles sizes as illustrated in the figure. This was due to large surface area of fine particles.

(iv) Effect of pH of the solution:

Earlier studies on heavy metal adsorption have shown that solution pH is the most important parameter affecting the adsorption process .

In order to establish the effect of pH on the adsorption of chromium(VI) ions,fixed bed adsorption studies at different pH values were conducted in the range of 1 to 7 **Fig.(9)** reveals that maximum adsorption capacity of Cr(VI) ions at pH =1 and significantly decrases with increase in pH values up to 7.

At lower pH, the biosorbent is positively charged due to protonation and dichromate ion exists as anion leading to an electrostatic attraction between them.Thus the uptake of Cr(VI) increased markedly with deceasing pH.Clear decrease in adsorption above pH 4 may be due to occupation of the adsorption sites by anionic species like $HCrO^{-2}{}_4$;$Cr_2O_7{}^{-2}$;$CrO_4{}^{-2}$ **;** etc. Which retards the approach of such ions further towards the sorbent surface(Boddu et al.,2003).

COMPETITIVE SEPARATION OF COPPER AND CHROMIUM(VI) :

The main objective of this part was to investigate the effect of other metals on chromium adsorption onto Sawdust.

Copper and Chromium were chosen due to their presence in several industrial wastewater and their toxicity.

Fig.10 show the breakthrough curves of copper and chromium(VI) on Sawdust ,it was clear that copper was higher removed than chromium(VI) at the early period of the adsorption process in a solution of 50% chromium and 50% copper at(pH 2),bed depth of(30 cm),particle size of (1.59mm),flowrate(2 l/h).

CONCLUSIONS :

The present study has led to the following conclusions:

1. Sawdust was effective in adsorbing heavy metal from wastewater.
2. In batch experiment the percent removal of Cr(VI) increases (66- 86 %) with increasing Sawdust dose (4 - 24 g/l).
3. Batch kinetics experiments showed that equilibrium time was about (120 min) with mechanical mixing by gar test at 120 rpm and at an initial concentration 50 ppm and adsorbent dose 8 gm/l.
4. The isotherm models (Langmiur, Freundlich and Langmiur- Freundlich) gave good fitting for the adsorption of Sawdust versus equilibrium concentration of chromium (VI). The correlation coefficients (R) obtained by "Statistica program" for these models were in the range of (95.6-95.91%).
5. In fixed bed experiment, the percent removal of chromium (VI) increases with increasing contact time, bed height, decreasing flow rate, reducing the pH of the solution.
6. The adsorption of chromium in the presence of copper ,showed that copper was higher affinity than chromium (VI) at the early period of the adsorption process in a mixture of (50% copper, 50% chromium (VI) at (pH=2,dp=1.59mm,flowrate=2l/h,bed depth=30cm).

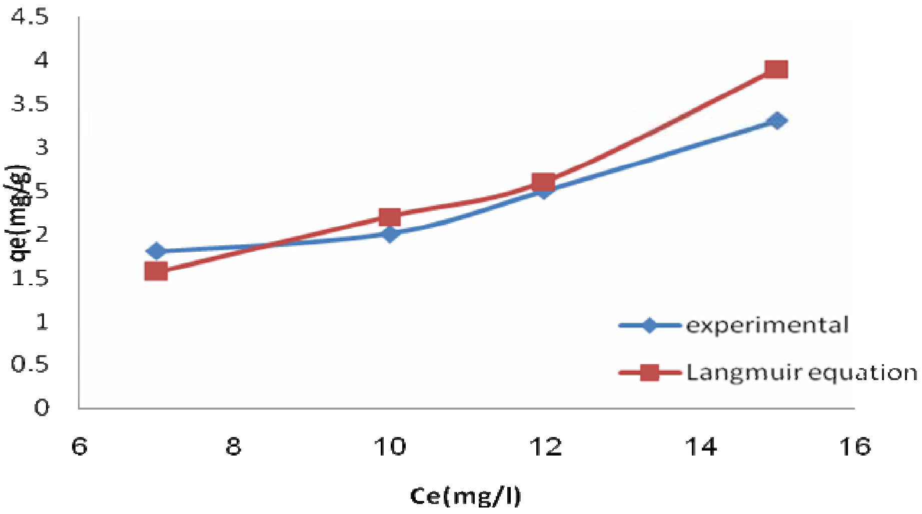

Fig. 2 Adsorption isotherm for Chromium on sawdust
(C_o=50mg/L, Temp. =25C^o,dp=1.59 mm)

Fig.3 Change in Chromium(VI) Concentration with Time of Batch Tests (C_o=50mg/L, Temp. =25C^o, particle size=1.59 mm)

Fig. 4 The Effect of Sawdust on Chromium(VI) Removal (Co=50mg/L, Temp. =25C^o, particle size=1.59mm)

Fig.5 Experimental Breakthrough Curves for Adsorption of chromium(VI) on sawdust at different flow rates (H=0.35 cm, d_p=0.35 cm,C_0=50 ppm)

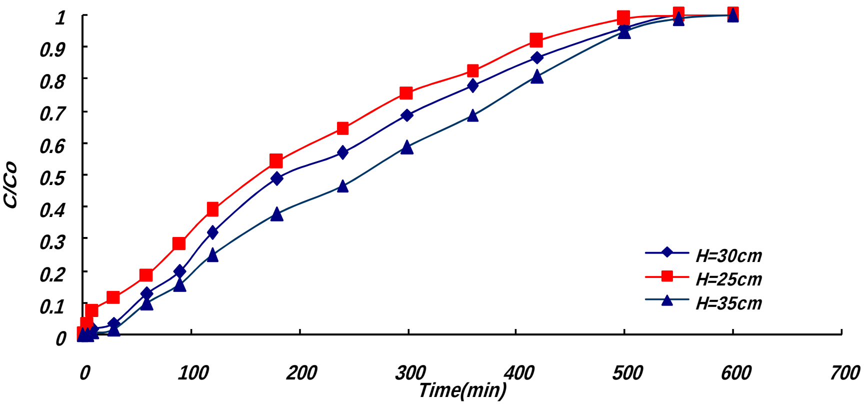

Fig.6 Experimental Breakthrough Curves for Adsorption of chromium(VI) at different bed depths (Q=2 l/hr, d_p=1.59mm,C_0=50 ppm)

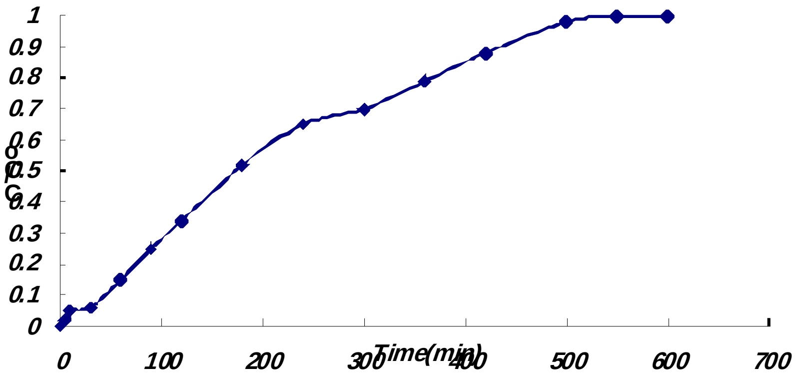

Fig.7 Experimental Breakthrough Curves for Adsorption of chromium(VI) at bed depth=60cm (Q=2 l/hr, d_p=1.59mm,C_0=50 ppm)

Fig.8 Experimental Breakthrough Curves for Adsorption of chromium(VI) on sawdust at different particle sizes(Q=2 l/hr, H=30 cm,C_0=50 ppm)

Fig.9 Experimental Breakthrough Curves for Adsorption of chromium(VI) on Sawdust at Different pH value (Q=2 l/hr, H=30 cm ,d_p=1.59 cm)

Fig.10 Experimental Breakthrough Curves for Adsorption of chromium(VI) and copper on Sawdust at (pH =2,Q=2 l/hr, H=30 cm ,d_p=1.59 cm)

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NOMENCLATURE :

a	Langmiur constant (L/mg)
b	Langmiur constant (mg/g)
C	Concentration of solute in solution at any time (mg/l)
C_e	Concentration of solute in solution at equilibrium (mg/l)
C_0	Initial concentration of adsorbate (mg/l)
k	Freundlich equilibrium constant indicative of adsorption capacity
m	Mass of solute adsorbent (g)
n	Freundlich constant indicative of adsorption intensity
H	Bed depth (m)
Q	Flow rate (l/h)
q_e	Amount of metal ion adsorbed at equilibrium (mg/g)
R	Correlation coefficient
t	Time (min)
x	Mass of solute adsorbed (mg)