

Short communication

## Adsorption of copper from aqueous solution on *Brassica cumpestris* (mustard oil cake)

Mohammad Ajmal, Rifaqat Ali Khan Rao\*, Moonis Ali Khan

Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202002, Uttar Pradesh, India

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### Abstract

The adsorption behavior of various heavy metals on mustard oil cake (MOC) was studied. The maximum adsorption of Cu(II) was observed followed by Zn(II), Cr(VI), Mn(II), Cd(II), Ni(II) and Pb(II). The adsorption of Cu(II) was found to be dependent on initial concentration of solution, pH, adsorbent dose, temperature and contact time. The adsorption followed pseudo-first-order and second-order kinetics but pseudo-second-order kinetic model was better obeyed since experimental data agreed well with theoretical data. Thermodynamic parameters were also evaluated. The adsorption process was found to be endothermic and spontaneous in nature. Attempts were also made to desorb Cu(II) from the adsorbent and regeneration of the spent adsorbent. The breakthrough and exhaustive capacities were found to be 5 and 10 mg g<sup>-1</sup>, respectively.

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### 1. Introduction

Industrialization has a tremendous impact on the concentration and distribution of heavy metals in the atmosphere, on the land and in the water bodies. The extent of this widespread but generally diffuse contamination has caused concern about its possible effects on the plants, animals and human beings. Among these contaminants, copper is a metal of concern. Copper is generally considered to be non-toxic for man but at concentration exceeding 5 mg l<sup>-1</sup> impart color and undesirable taste to water. The World Health Organization's guideline for drinking water based on its staining properties is 1 mg l<sup>-1</sup> [1]. Beyond the permissible level (5 mg l<sup>-1</sup>), copper causes acute and chronic disorders in human beings such as gastrointestinal catarrh, cramps in the calves, hemochromatosis and skin dermatitis brasschills, usually accompanied by high fever [2,3]. Industries discharging copper in the wastewater are electroplating industries, pulp and paper mills, fertilizer plants, steel work foundries, petroleum refineries, aircraft

plating and finishing, motor vehicles and non-ferrous metal works [4–6].

Processes generally used for the removal of Cu(II) from wastewater include precipitation, evaporation, reverse osmosis and ion exchange. But most of these processes are economically non-feasible for small scale industries to treat the waste effluents. The adsorption process has been found to be economically appealing for the removal of heavy metals from wastewater. For the treatment of copper rich effluents at the solid-solution interface, several adsorbents have been used earlier [7–13]. The adsorption behavior of orange fruit peel, sawdust, kyanite and rice husk for the removal and recovery of Hg(II), Cr(VI), Ni(II), Cu(II), Cd(II), Pb(II), Zn(II) and Mg(II) from rivers and industrial wastewater have been studied in our laboratory [14–18].

In the present study, a new adsorbent mustard oil cake (MOC) prepared from the seeds of *Brassica cumpestris* (mustard) is used. It is a valuable by-product left after the extraction of oil and is known as mustard oil cake. It contains significant amount of proteins, of value as animal feed if edible and as nitrogenous manure otherwise. The chemical

\* Corresponding author. Tel.: +91 571 2700920x3000.

E-mail address: rakrao2000@yahoo.com (R.A.K. Rao).

composition of mustard oil cake shows nitrogen (4.5%) and phosphorous penta oxide (1.5%) [19].

## 2. Material and method

### 2.1. Adsorbent

Oil was extracted from the *B. cumpestris* (mustard) seeds and waste matter left after extraction is known as mustard oil cake. The mustard oil cake was treated with hot double distilled water in order to remove the oil and finally dried in air over at 60–65 °C for 24 h. After drying, the adsorbent was sieved through 40–60 mesh size (BSS) and used as such.

### 2.2. Adsorbate solution

Stock solution of Cu(II) was prepared (1000 mg l<sup>-1</sup>) by dissolving the desired quantity of copper nitrate trihydrate (AR grade) in distilled water. Solutions of other metal ions were prepared (1000 mg l<sup>-1</sup>) by dissolving their chlorides or nitrates.

### 2.3. Adsorption studies

Adsorption studies were carried out by batch process. 0.5 g adsorbent was placed in a conical flask in which 50 ml solution of metal ion of desired concentration was added and the mixture was shaken in shaker. The mixture was then filtered and final concentration of metal ion was determined in the filtrate by atomic absorption spectrophotometer (GBC 902). The amount of metal ions adsorbed was calculated by subtracting final concentration from initial concentration. All the experiments were carried out in triplicate and mean concentration was calculated by averaging them. The relative standard deviation (R.S.D.) for each sample was calculated. The values of R.S.D. (on percent basis) in all the experiments were found to be in the range 0.548–1.252%.

### 2.4. Effect of pH

The effect of pH on the adsorption of Cu(II) was studied as follows: 100 ml of Cu(II) solution was taken in a beaker. The pH of solution was adjusted by adding dilute solution of hydrochloric acid or sodium hydroxide. The concentration of Cu(II) in this solution was then determined (initial concentration). Fifty millilitres of this solution was taken in a conical flask and treated with 0.5 g of adsorbent and after equilibrium, the final concentration of Cu(II) was determined.

### 2.5. Effect of time

A series of 250 ml conical flask, each having 0.5 g adsorbent and 50 ml solution (of known Cu(II) concentrations)

were shaken in a shaker incubator and at the predetermined intervals, the solution of the specified flask was taken out and filtered. The concentration of Cu(II) in the filtrate was determined by atomic absorption spectrophotometer (GBC 902 model). The amount of Cu(II) adsorbed in each case was then determined as described earlier.

### 2.6. Effect adsorbent dose

A series of 250 ml conical flasks each containing 50 ml of Cu(II) solution of 50 mg l<sup>-1</sup> concentration were treated at 20 °C with varying amount of adsorbent (0.1–1.0 g) at pH 4. The flasks were shaken in a shaker incubator and after equilibrium, the solutions were filtered. The amount of Cu(II) in the filtrate was then determined by atomic absorption spectrophotometer. The amount of Cu(II) adsorbed in each case was then calculated as described above. The same procedure was repeated at 30 and 40 °C.

### 2.7. Breakthrough capacity

0.5 g of adsorbent was taken in a glass column (0.6 cm internal diameter) with glass wool support. One litre of Cu(II) solution with 50 mg l<sup>-1</sup> initial concentrations ( $C_0$ ) was then passed through the column with a flow rate of 1 ml min<sup>-1</sup>. The effluent was collected in 50 ml fractions and the amount of Cu(II),  $C$  was determined in each fraction with the help of atomic absorption spectrophotometer. The breakthrough curve was obtained by plotting  $C/C_0$  versus volume of the effluent.

### 2.8. Desorption studies

Desorption of Cu(II) was carried out as follows: 0.5 g of adsorbent was treated with 50 ml Cu(II) solution (50 mg l<sup>-1</sup>) in a conical flask. The solution was filtered after 24 h. The adsorbent was then washed several times with distilled water to remove any excess of Cu(II). It was then treated with 50 ml of 0.1 M sodium chloride solution and then filtered after 24 h. The filtrate was analyzed for Cu(II) desorbed. The same procedure was repeated with potassium sulphate and hydrochloric acid solutions.

### 2.9. Regeneration studies

0.5 g of adsorbent was treated with 50 ml Cu(II) solution (50 mg l<sup>-1</sup>) in a conical flask and after equilibrium, it was filtered. The adsorbent was then treated with 50 ml hydrochloric acid solution (0.05 M) for 24 h. It was filtered and filtrate was analyzed for Cu(II) desorbed. The adsorbent was washed several times with distilled water in order to remove excess acid. It was again treated with 50 ml of Cu(II) solution and the above procedure was repeated a number of times (five times or cycles). The same procedure was repeated with 0.1 M hydrochloric acid solution.

Table 1  
Adsorption of different metal ions on to mustard oil cake (MOC)

S. no.	Metal ions	Adsorption (mmols g <sup>-1</sup> )
1	Zn(II)	0.691
2	Mn(II)	0.582
3	Cu(II)	0.717
4	Cr(VI)	0.675
5	Cd(II)	0.396
6	Pb(II)	0.183
7	Ni(II)	0.357

### 3. Result and discussion

The adsorption behavior of different metal ions on mustard oil cake is shown in Table 1. The adsorption or metal uptake (mmols g<sup>-1</sup>) of Cu(II) was found to be maximum followed by Zn(II), Cr(VI), Mn(II), Cd(II), Ni(II) and Pb(II).

#### 3.1. Effect of time and initial concentration

The effect of time and amount adsorbed ( $x/m$ ) by MOC is presented in Fig. 1. The adsorption of Cu(II) has been shown to increase with time and attains a maximum value at 20 min and then remains almost constant for 50 mg l<sup>-1</sup> initial Cu(II) concentration, but below this concentration, the maximum adsorption occurs much earlier. When initial Cu(II) concentration is increased from 5 to 50 mg l<sup>-1</sup>, the amount adsorbed increases from 8.8 to 96 mg l<sup>-1</sup>, showing that adsorption of Cu(II) depends upon the initial concentration because amount of Cu(II) adsorbed increases by increasing the initial concentration.

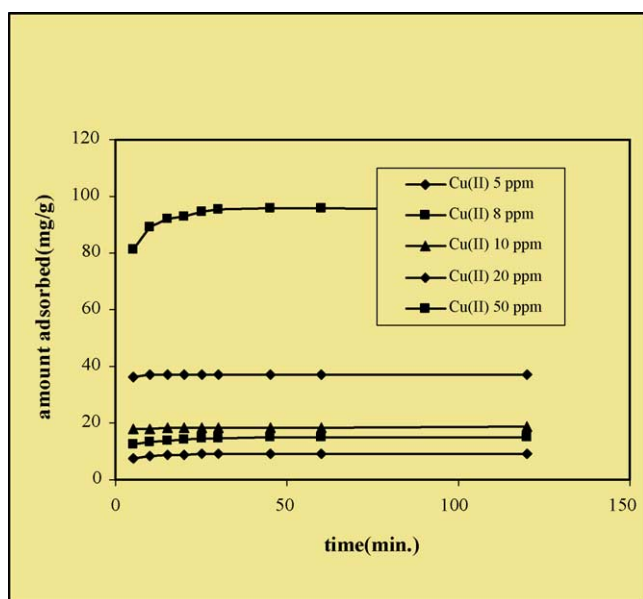


Fig. 1. Effect of time and initial concentration of Cu(II).

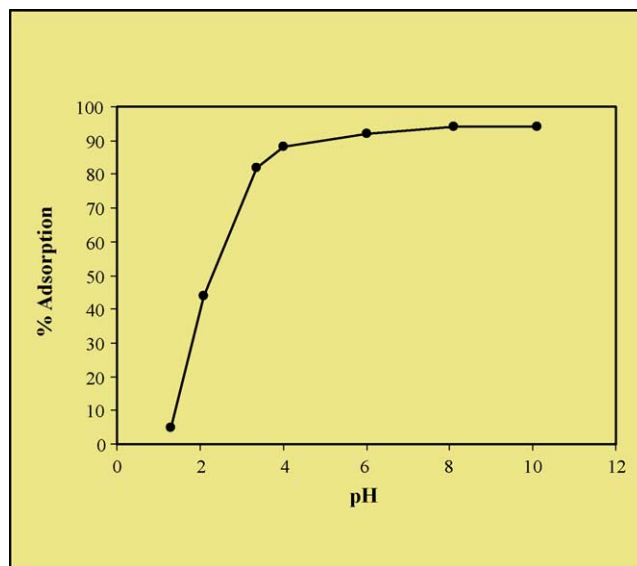


Fig. 2. Effect of pH.

#### 3.2. Effect of pH

The effect of pH on the adsorption of Cu(II) on MOC is shown in Fig. 2. The percentage adsorption varies from 44 to 94%. When pH is increased from 2 to 10 at 50 mg l<sup>-1</sup> initial concentrations, the maximum percentage adsorption is observed between pH 3 and 4. At this pH, there are two species of Cu(II) present in the solution [15]:

- Cu(II) (large quantity);
- CuOH (small quantity).

The maximum adsorption at pH 3–4 indicates that Cu(II) ions are predominantly adsorbed on MOC (since Cu(II) ions are present in large quantity in this pH range) either by ion exchange or by hydrogen bonding. The percent adsorption increases slowly with increasing pH and becomes constant above pH 6 due to the precipitation of Cu(II) as Cu(OH)<sub>2</sub>.

#### 3.3. Adsorption isotherms

The adsorption isotherm data were analyzed with Langmuir and Freundlich isotherms [14]. The values of  $\theta$  and  $b$  were calculated from the slope and intercept of the linear plots of  $1/(x/m)$  versus  $1/C_e$  (Table 2).

This essential feature of the Langmuir isotherm can be expressed in terms of dimensionless constant separation or equilibrium parameter ( $R_L$ ), which is defined as:

$$R_L = \frac{1}{1 + bC_0} \quad (1)$$

where  $C_0$  is the initial metal ion concentration (mg l<sup>-1</sup>) and  $b$  is the Langmuir constant. The values of  $R_L$  reported in Table 2 at different temperatures are less than unity ( $R_L < 1$ ) showing favorable adsorption of Cu(II) on MOC [20]. The values of  $K_f$  and  $n$  were calculated from the intercept and slope of the

Table 2

Langmuir and Freundlich constants at different temperature for the adsorption of Cu(II) on to MOC

Temperature (°C)	Langmuir isotherms					Freundlich isotherms			
	$\theta^0 b$ (l g <sup>-1</sup> )	$\theta^0$ (mg g <sup>-1</sup> )	$b$ (l mg <sup>-1</sup> )	$R^2$	$R_L$	Log $K_f$	$K_f$	$n$	$R^2$
20	63.350	454.54	0.139	0.9901	0.887	1.8512	70.99	1.82	0.9933
30	78.125	434.78	0.179	0.9842	0.848	1.9515	89.43	2.09	0.9988
40	74.620	714.28	0.104	0.9853	0.905	1.9539	89.92	1.69	0.9692

Freundlich plots. These values are reported in Table 2. The values of  $n$  between 1 and 10 represent beneficial adsorption [21].

### 3.4. Effect of temperature

The temperature range used in this study was 20–40 °C. The values of equilibrium constants ( $K_c$ ) at 20, 30 and 40 °C were calculated from the following relation [22]:

$$K_c = \frac{C_{Ac}}{C_e} \quad (2)$$

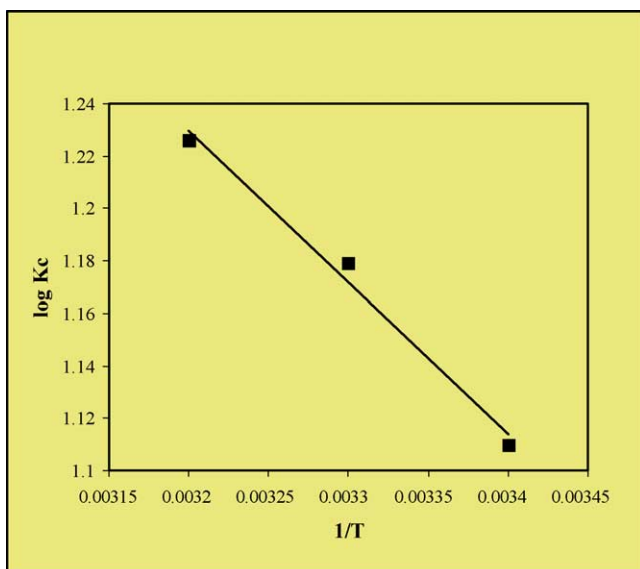
where  $C_{Ac}$  and  $C_e$  are the equilibrium concentrations (mg l<sup>-1</sup>) of Cu(II) on the adsorbent and in solution, respectively.

$$\Delta G^0 = -RT \ln K_c \quad (3)$$

where  $T$  is the absolute temperature,  $R$  gas constant and  $\Delta G^0$  is the standard free energy change. The values of enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) were calculated from the following relation:

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (4)$$

$\Delta S^0$  and  $\Delta H^0$  were calculated from the slope and intercept of linear plot of  $\log K_c$  versus  $1/T$  (Fig. 3). Table 3 shows the

Fig. 3. Plot of  $\log K_c$  vs.  $1/T$ .

values of  $K_c$ ,  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$ . The positive value of  $\Delta H^0$  indicates that the process is endothermic. The negative values of  $\Delta G^0$  show that process is spontaneous and spontaneity increases with increase in temperature. The positive value of  $\Delta S^0$  suggests an increase randomness at the solid–liquid interface during adsorption.

### 3.5. Adsorption kinetics

The rate constants were calculated by using Lagergren first-order and pseudo-second-order kinetic equations. Lagergren first-order expression is given by equation:

$$\log(q_e - q) = \log q_e - \frac{K_1}{2.303t} \quad (5)$$

where  $q_e$  is the amount adsorbed at equilibrium,  $q$  the amount adsorbed at time  $t$  and  $K_1$  is the adsorption rate constant. The linear plot of  $\log(q_e - q)$  versus  $t$  is observed (Fig. 4). The

Table 3

Thermodynamics parameters at different temperature for the adsorption of Cu(II) on MOC

Temperature (°C)	$K_c$	$\Delta G^0$ (kJ mol <sup>-1</sup> )	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (kJ mol <sup>-1</sup> )
20	12.88	-6.247		
30	15.13	-6.842	11.105	0.059
40	16.85	-7.337		

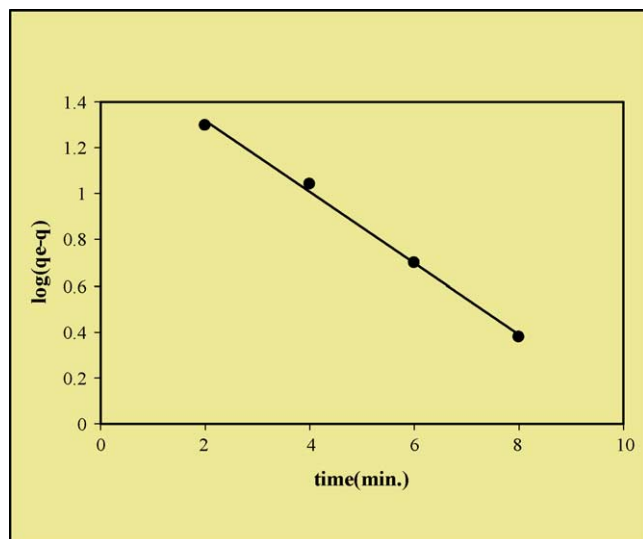


Fig. 4. Lagergren pseudo-first-order kinetics.

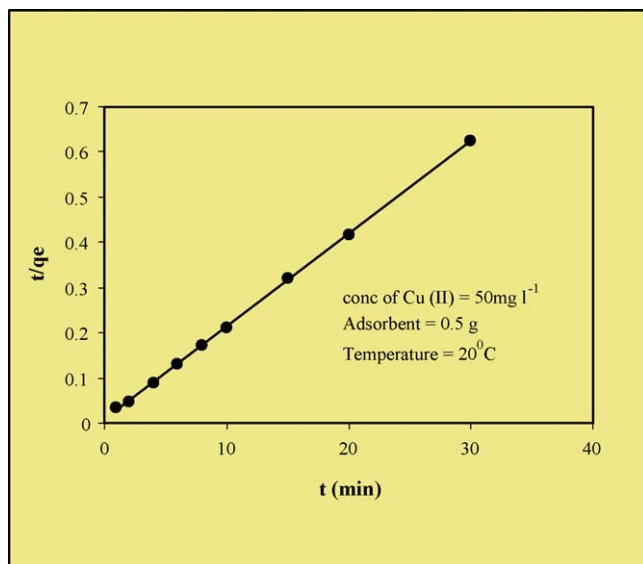


Fig. 5. Pseudo-second-order kinetics.

regression coefficient ( $R^2$ ) in this case is 0.9971. The value of rate constant  $K_1$  as determined from the slope of the line was  $0.357 \text{ min}^{-1}$  the pseudo-second-order adsorption kinetic rate equation is given as:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e t} \quad (6)$$

where  $K_2$  is the adsorption rate constant of pseudo-second-order kinetics ( $\text{g mg}^{-1} \text{ min}^{-1}$ ). The value of  $K_2$  was calculated from the slope of the linear plot of  $t/q$  versus  $t$  (Fig. 5). A comparison of the experimental sorption capacities and calculated values obtained from Eqs. (5) and (6) shows that  $q_e$  (theoretical) value calculated from the pseudo-first-order kinetic model ( $42.6 \text{ mg g}^{-1}$ ) differed largely from  $q_e$  (experimental) value ( $48.0 \text{ mg g}^{-1}$ ). In pseudo-second-order kinetics, the calculated  $q_e$  (theoretical) value ( $48.0 \text{ mg g}^{-1}$ ) was found to be very close to  $q_e$  (experimental) value ( $48.0 \text{ mg g}^{-1}$ ) and also the high value (0.9998) of the correlation coefficient ( $R^2$ ) confirmed the applicability of the pseudo-second-order kinetics.

### 3.6. Breakthrough capacity

The breakthrough curve for  $50 \text{ mg l}^{-1}$  initial Cu(II) concentration and a flow rate of  $1 \text{ ml min}^{-1}$  with  $0.5 \text{ g}$  adsorbent is shown in Fig. 6. The breakthrough curve showed that

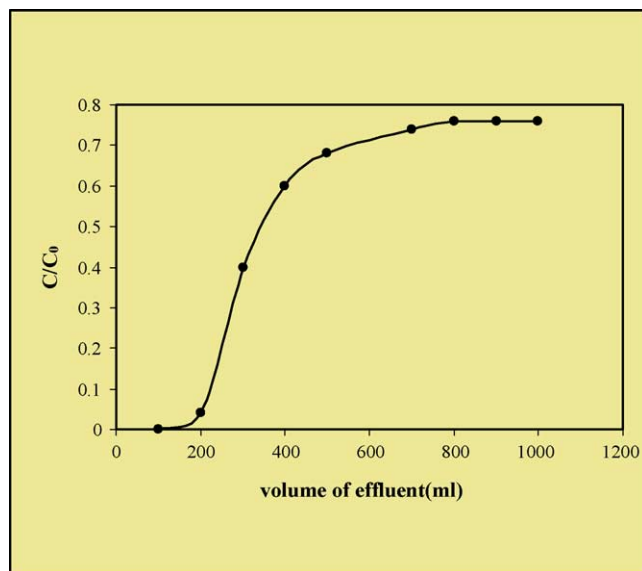


Fig. 6. Breakthrough capacity.

50 ml of the solution (corresponding to  $2.5 \text{ mg Cu(II)}$ ) could be passed through the column without detecting Cu(II) in the effluent. The breakthrough and exhaustive capacities were determined as  $5$  and  $10 \text{ mg g}^{-1}$ , respectively.

### 3.7. Desorption studies

In order to make the adsorption process more economical, it is important to desorb and regenerate the spent adsorbent. The desorption studies were carried out by batch process using NaCl,  $\text{K}_2\text{SO}_4$  and HCl solutions of different concentrations. The results are reported in Table 4. Desorption of Cu(II) with NaCl or  $\text{K}_2\text{SO}_4$  is negligible showing that Cu(II) is strongly adsorbed on MOC. This is important because Cu(II) adsorbed by MOC will not be exchanged by NaCl or  $\text{K}_2\text{SO}_4$  if MOC is to be used to sequester Cu ions in soil since appreciable amount of these salts are usually present in the soil. However, desorption up to the extent of 67% could be achieved when  $0.1 \text{ M}$  hydrochloric acid solution was used as eluent. Desorption of metal ions with acid solution indicates that adsorption of Cu(II) is via ion-exchange process.

Attempts were made to regenerate the spent adsorbent with  $0.05$  and  $0.1 \text{ M}$  hydrochloric acid solutions. The results

Table 4  
Desorption of Cu(II) by various eluents

S. no.	Amount of Cu(II) adsorbed (mg)/0.5g adsorbent	Amount of Cu(II) recovered (mg)	Recovery (%)	Eluent used
1	45	1.1	2.2	0.1 M NaCl
2	42.8	1.2	2.8	1.0 M NaCl
3	42.1	2.0	4.0	0.1 M $\text{K}_2\text{SO}_4$
4	44.2	28	63.3	0.05 M HCl
5	43	29	67.4	0.1 M HCl

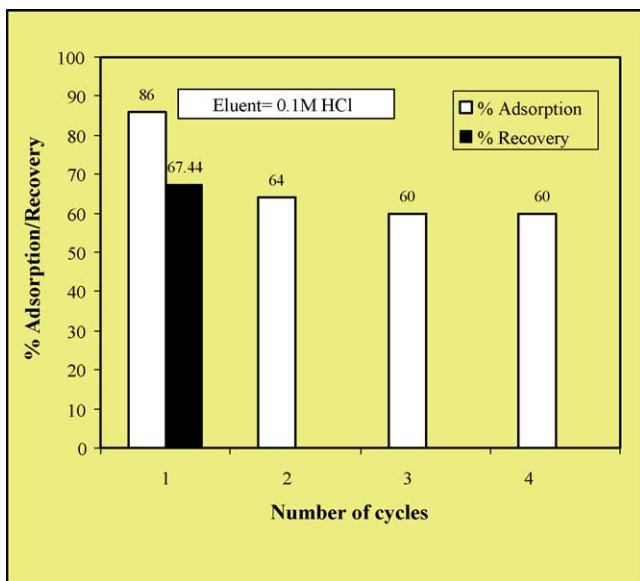


Fig. 7. Regeneration studies by batch process.

were almost similar. Fig. 7 shows that percent adsorption decreases from 86 to 64% after first regeneration and recovery of Cu(II) is 67.4%. The percent adsorption then remains almost constant (64–60%) in the subsequent cycles. The remarkable decreases in the first regeneration cycle indicates that perhaps certain adsorption sites or functional groups are decomposed or destroyed by hydrochloric acid and hence it is expected that Cu(II) is weakly adsorbed in the second, third and fourth cycle. However, 60% adsorption could be achieved up to fourth regeneration cycle.

#### 4. Conclusions

Mustard oil cake is a low cost material abundantly available in India. It is used as manure in agriculture to provide nitrogen and phosphorous (essential plant nutrients). Its adsorption properties could be utilized to sequester Cu(II) ions in the soil. The order of adsorption of various heavy metals on MOC is Cu(II) > Zn(II) > Cr(VI) > Mn(II) > Cd(II) > Ni(II) > Pb(II).

The adsorption of Cu(II) is pH dependent and maximum adsorption occurs at pH 3–4.

The adsorption follows pseudo-first- and pseudo-second-order kinetics but pseudo-second-order kinetic equation is better obeyed.

The adsorption process is endothermic and spontaneous in nature. Breakthrough capacity shows that 50 ml of water (corresponding to 2.5 mg of Cu(II)) can be treated without detecting Cu(II) in the effluent.

The Cu(II) ions are strongly adsorbed on MOC and cannot be recovered with various neutral salt solutions like NaCl, K<sub>2</sub>SO<sub>4</sub>, etc. The recovery of Cu(II) can be made to some extent with dilute hydrochloric acid solution but treatment of

MOC with hydrochloric acid remarkably reduces the capacity of adsorbent.

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