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Removal and recovery of Cu(II), Cd(II) and Pb(II) ions from single and multimetal systems by batch and column operation on neem oil cake (NOC)

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Abstract

NOC, a byproduct obtained after extraction of oil from neem fruit was used as an adsorbent for the removal of Pb(II) from wastewater. The adsorption of Pb(II) was found to be maximum (98%) at pH 4. The lower value of Langmuir constant (b) indicates strong binding of Pb(II) on NOC surface. The Freundlich constant n indicates beneficial adsorption. Thermodynamic parameters (ΔH° and ΔG°) suggest endothermic and spontaneous process. Kinetic studies show better applicability of second order kinetic model. The practical utility of NOC was demonstrated by removing Pb(II) along with Cd(II) and Cu(II) from single metal and multimetal systems by batch and column process. It was found that removal efficiency of NOC was better by column operation in multimetal system. The breakthrough capacities of Cu(II), Cd(II) and Pb(II) on NOC are found to be 10, 15 and 30 mg/g, respectively.

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1. Introduction

Industrial effluents are loaded with toxic heavy metals beyond permissible limit, causing hazardous effects to biota. The toxicity of these pollutants have led to enforce stringent standards on the maximum allowable limits for their disposal into open landscapes and water bodies [1]. Heavy metals are non-degradable and tend to accumulate in human body causing various disorders [2]. Textile, electroplating, painting dyeing, surface treatment industries, etc. are the main source of heavy metal pollution [3].

Many conventional techniques have been used to reduce the concentration of heavy metals present in wastewater. Chemical precipitation and filtration, chemical oxidation and reduction, electrochemical treatment, reverse osmosis, solvent extraction and evaporation all shows several disadvantages, such as high cost, incomplete metal removal, low selectivity, high energy

requirements and generation of toxic slurries that are difficult to be eliminated [4]. Ion-exchange is a highly popular method and has been widely practiced in industrial wastewater treatment process, but the application of such process is often restricted because it cannot guarantee the metal concentration limits required by regulatory standards, especially when metal concentration in the effluent are below 100 mg/l [5,6].

Adsorption is a well established technique for the removal of heavy metals present in traces. The practical applicability of heavy metal adsorption is most effectively carried out in packed bed column, as it efficiently utilize the sorbent capacity and results in a better quality of effluent [7]. Numerous studies have reported adsorption of metals by materials of diverse biological origin, these have remained limited to single species of heavy metal ions and very little information is available for binary and multimetal adsorption systems [8,9]. Wastewaters, however contain multiple metals, which are likely to cause interactive effects depending on the number of metals competing for binding sites, the combination of these metals, initial concentrations, the equilibrium steady state concentration of different metal ion species, limitations presented by the binding sites and the nature and quality of biosorbent [10,11]. Among the few

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multimetal biosorption systems investigated are the removal of Ni and Cr by *Cyanobacterium Microcystis* [12], Ni and Cu by *Sphagnum* moss peat [13], Cu and Cd by bacterium *Arthrobacter* [14], Cd, Pb and Zn by bacterium *Alteromonas* [15], Cd, Cu, Ni, Zn by BGH [16].

This study has demonstrated the adsorption properties of neem oil cake (NOC), the residue left after the extraction of oil from neem fruit. Neem (*Azadirachta indica*), an evergreen tree endemic to the Indian subcontinent. It is used in ayurvedic, unani and folklore traditional medicines, in the treatment of wide range of applications. Formulations made of neem oil find wide usage as a bio-pesticide for organic farming [17,30]. The C/N ratio in NOC is very less that means after its use as an adsorbent it will take no time to decompose [18]. This is an additional advantage of NOC that makes it an eco-friendly adsorbent. In our earlier paper we have explored the adsorption of Cu(II) and Cd(II) on NOC. In this paper adsorption and desorption efficiency of NOC for single metal system of Pb(II) and multimetal system of Pb(II), Cd(II) and Cu(II) in double distilled water (DDW) and tap water are studied by applying batch and column processes.

2. Material and methods

2.1. Adsorbent

Oil was extracted from the fruit of neem (*A. indica*) and waste matter left after extraction is known as neem oil cake (NOC). The NOC was treated with hot double distilled water (DDW) in order to remove the traces of oil and finally dried in open-air oven at 60–65 °C for 24 h. After drying, the adsorbent was sieved through 50–100 (BSS) mesh size and used as such.

2.2. Adsorbate solution

Single-component stock solutions of Cu(II), Cd(II) and Pb(II) were prepared (1000 mg/l) by dissolving the desired quantity of their nitrate salts (A.R. grade) in DDW.

2.3. Adsorption studies

Adsorption studies were carried out by batch and column process. In batch process 0.5 g adsorbent was placed in conical flask in which 50 ml solution of metal ion of desired concentration was added and the mixture was shaken in temperature controlled shaker incubator for 24 h at 120-rev./min. The mixture was then filtered using Watman filter paper number 41 and final concentration of metal ion was determined in the filtrate by atomic absorption spectrophotometer (AAS) (GBC 902). In the column process 0.5 g of adsorbent was placed in a glass column (0.6 cm internal diameter) with glass wool support. Metal solution was passed through the column with a flow rate of 1 ml/min. The effluent was collected in fractions and amount of metal ion in each fraction was determined by AAS. The amount of metal ions adsorbed was calculated by subtracting final concentration from initial concentration.

2.4. Effect of pH

The effect of pH on the adsorption of Pb(II) was studied by batch process as follows: 100 ml of metal solution was taken in beaker. The pH of solution was adjusted by adding dilute solution of HCl and NaOH. The concentration of Pb(II) in this solution was then determined (initial concentration). Fifty millilitres of this solution was taken in conical flask and treated with 0.5 g adsorbent and after equilibrium, the final concentration of Pb(II) was determined.

2.5. Effect of contact time

A series of 250 ml conical flasks, each having 0.5 g adsorbent and 50 ml solution (of known Pb(II) concentration) were shaken in temperature controlled shaker incubator at 120-rev./min and at the predetermined intervals, the solution of the specified flask was taken out and filtered. The concentration of Pb(II) in the filtrate was determined by AAS. The amount of Pb(II) adsorbed in each case was then determined as described earlier.

2.6. Effect of adsorbent dose

A series of 250 ml conical flasks each containing 50 ml of metal solution (of known metal concentration) were treated at different temperatures with varying amount of adsorbent (0.1–0.8 g). The flasks were shaken in temperature controlled shaker incubator at 120-rev./min and after equilibrium the solutions were filtered. The amount of Pb(II) in filtrate was then determined by AAS. The amount of Pb(II) adsorbed in each case was calculated as above.

2.7. Breakthrough capacity

0.5 g of adsorbent was taken in glass column (0.6 cm internal diameter) with glass wool support. One thousand millilitres of metal solution with 50 mg/l initial concentration (C_0) was passed through the column with a flow rate of 1 ml/min. The effluent was collected in 50 ml fractions and the amount of metal (C) was determined in each fraction by AAS. The breakthrough curve of each metal was obtained by plotting C/C_0 versus volume of the effluent. In order to see the desorption behavior, the exhausted column was washed several times with double distilled water to remove excess of metal ions from the column, then 0.1 M HCl was passed separately through each column containing adsorbed Cu(II), Cd(II) and Pb(II). The metal ions eluted were collected in 10 ml fractions. The flow rate was maintained at 1 ml/min in each case.

2.8. Desorption studies

Desorption studies were carried out by both batch and column process. In batch process 50 ml solution of each Cu(II), Cd(II) and Pb(II) was treated separately with 0.5 g of adsorbent in temperature controlled shaker incubator at 120-rev./min for 24 h. Similarly 50 ml of the mixture of metal ions (containing 20 mg/l each of Cu(II), Cd(II) and Pb(II)) (ratio 1:1:1) in DDW and the

mixture of Cu(II), Cd(II) and Pb(II) (20 mg/l each) (ratio 1:1:1) in tap water were treated in the same way with the adsorbent. The adsorbent in each flask was washed several times with DDW to remove excess of metal ions. The experiment was carried out in duplicate. The adsorbent after washing was treated with 50 ml of water and kept for 24 h. It was then analyzed for any leaching of metal ions and it was found that no metal ions were released from the adsorbent. The adsorbent in another flask was treated with 50 ml 0.1 M HCl. The flasks were shaken in temperature controlled shaker incubator at 120-rev./min (to desorb Cu(II), Cd(II) and Pb(II)) for 24 h. The solutions were then filtered by using Watman filter paper number 41. The filtrates were analyzed for metals desorbed.

In column process 0.5 g of adsorbent was taken in glass column (0.6 cm internal diameter) with glass wool support. Fifty millilitres solution of Cu(II), Cd(II) and Pb(II) (50 mg/l each), 50 ml mixture of Cu(II), Cd(II) and Pb(II) containing 20 mg/l each (ratio 1:1:1) in DDW and mixture of Cu(II), Cd(II) and Pb(II) containing 20 mg/l each (ratio 1:1:1) in tap water were passed through each column at 1 ml/min flow rate. The adsorbent in each column was washed several times by DDW in order to remove traces of metal ions remained unadsorbed. 0.1 M HCl solution was then passed separately through each column as an eluent. The effluent was collected in 10 ml fractions in each case with a flow rate of 1 ml/min and the metal ions desorbed were determined in each fraction.

2.9. Quality assurance and quality control

To make sure that no metal ions were released to the solution from the adsorbent, an equilibrium test was performed using adsorbent (NOC) in DDW. For assuring quality in the adsorption studies distilled water blank and two duplicates were included in the experiments.

To ensure accuracy after each set of five samples, a standard was analyzed to ensure that drift had not occurred.

The samples were analyzed in triplicate by AAS. Average of the values obtained gives mean concentration of the sample. The percent relative standard deviation (R.S.D.) for samples was calculated by dividing standard deviation of the sample with the average of the sample multiplied by 100. If the value of percent R.S.D. for any sample was greater than 10% the data were declared unusable.

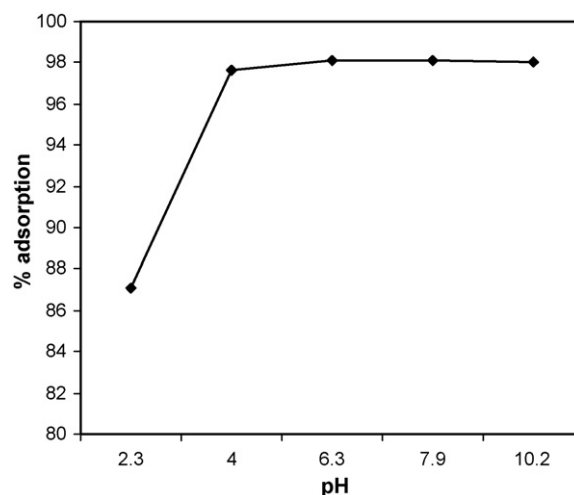


Fig. 1. Effect of pH on the adsorption of Pb(II) on NOC.

3. Result and discussions

3.1. Effect of initial concentration

Initial metal concentration provides important driving force to overcome all mass transfer resistances of the metal between the aqueous and solid phase [19]. The increase in the initial concentration of Pb(II) solution at room temperature (i.e. 32 °C) increases the adsorption capacity (Table 1). Table 1 summaries the results of the adsorption capacity accuracy test.

3.2. Effect of pH

The percentage adsorption of Pb(II) on NOC increases by increase in pH, attaining optimum at pH 4 (Fig. 1). Availability of negatively charged groups on the adsorbent surface is necessary for the sorption of metals to proceed [20] at pH 2 the adsorption is likely as there is a net positive charge in the adsorption system due to H⁺ and H₃O⁺. In such system H⁺ compete with metal ions [21] resulting in active sites to become protonated to the virtual exclusion of metal binding on the adsorbent surface [22]. This means that at higher H⁺ concentration, the adsorbent surface becomes more positively charged thus reducing the attraction between adsorbent and metal cations [23]. In

Table 1
Reproducibility test for adsorption capacity of Pb(II) on NOC

Initial conc. C ₀ (mg/l)	Average final conc. C _e (mg/l)	Average adsorption capacity q _e (mg/g)	Standard deviation of q _e	Relative standard deviation of q _e
10	0.1667	0.9833	0.0058	0.590
20	0.4333	1.9567	0.0058	0.296
30	0.6333	2.9367	0.0058	0.197
40	0.7667	3.9233	0.0153	0.390
50	0.7667	4.9233	0.0058	0.118
60	0.8000	5.9200	0.0082	0.138
70	0.8000	6.9200	0.0082	0.118
90	0.8333	8.9167	0.0115	0.129
100	0.8667	9.9133	0.0153	0.154

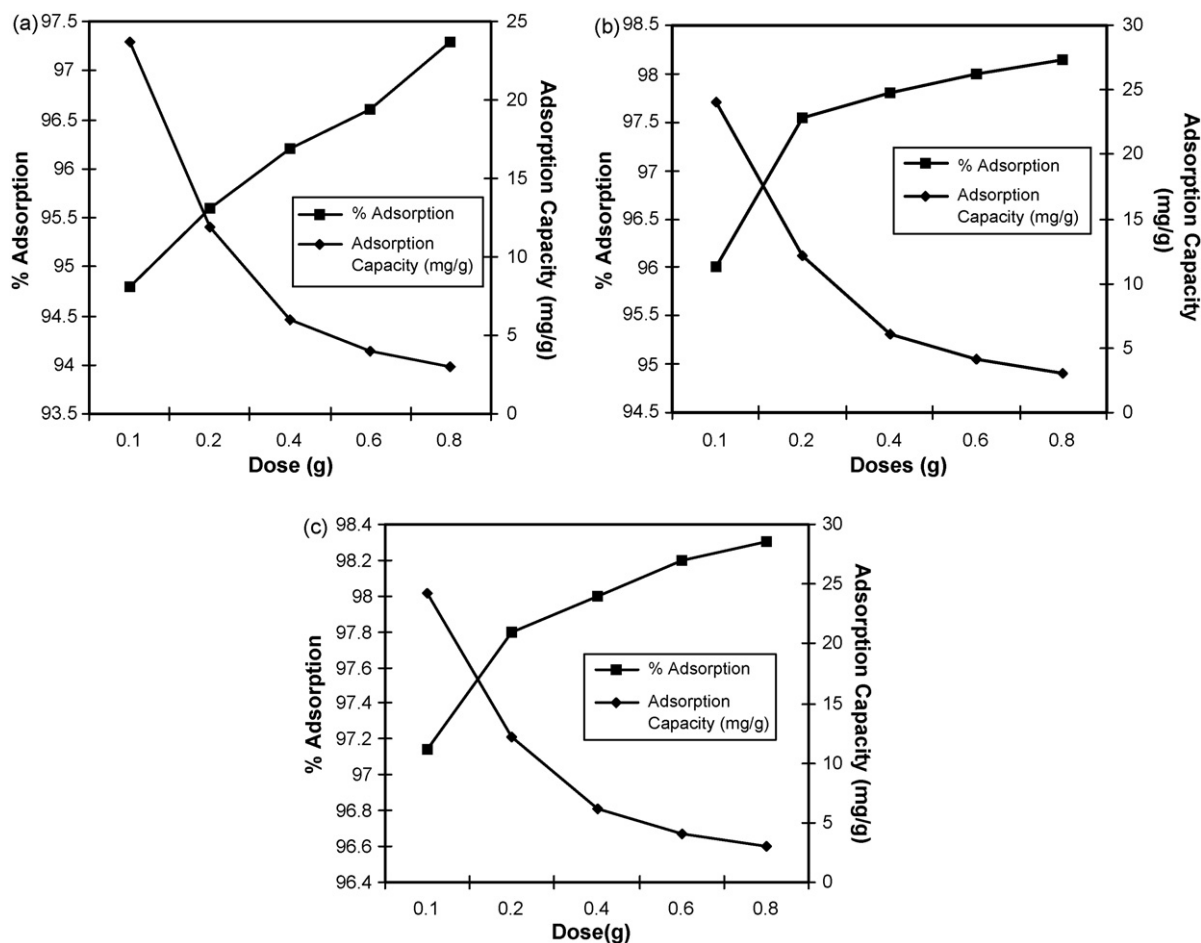


Fig. 2. (a) Effect of adsorption dose on % adsorption and adsorption capacity of Pb(II) NOC at 30 °C. (b) Effect of adsorption dose on the % adsorption and adsorption capacity of Pb(II) on NOC at 40 °C. (c) Effect of adsorbent dose on the % adsorption and adsorption capacity of Pb(II) on NOC at 50 °C.

contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake [24]. The metal adsorption noted to increase significantly by increasing pH, thus Pb(II) with 50 mg/l (initial concentration) at pH 4 shows 98% (maximum) adsorption. With further increase in pH, the solubility of metals decreases resulting in their precipitation as hydroxide with no significant increase in percentage adsorption.

3.3. Effect of adsorbent doses

The adsorption capacity (mg/g) and percentage (%) adsorption of Pb(II) by varying the dose of NOC at different temperatures is shown in Fig. 2a–c. The % adsorption increases as the adsorbent dose of NOC is increased for Pb(II). However, increase in temperature has no significant effect on % adsorption. It may be concluded that by increasing the adsorbent dose, the removal efficiency of NOC increases, while adsorption density/capacity decreases. The decrease in adsorption density may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process where as the number of sites available for adsorption increases by increasing the adsorbent doses and that results in the increase in removal efficiency [25].

3.4. Adsorption isotherms

The adsorption isotherms are well described by the Langmuir and Freundlich isotherms for a wide range of adsorbate concentration.

The Langmuir isotherm is given by equation:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} \times C_e \quad (1)$$

where C_e is the equilibrium concentration of adsorbate (mg/l); q_e the adsorption capacity (mg/g); b and q_m are the Langmuir constants.

The values of Langmuir constants b and q_m were calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e (Fig. 3). The coefficient b in Langmuir equation is a measure of the stability of the complex formed between metal ions and adsorbent under specified experimental conditions [26].

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

$$R_L = \frac{1}{1 + bC_o} \quad (2)$$

Table 2
Langmuir and Freundlich constants for the adsorption of Pb(II) on NOC

Metal ions	Langmuir constants					Freundlich constants		
	q_m (mg/g)	b (l/mg)	bq_m (l/g)	R^2	R_L	K_f (mg/g)	n	R^2
Pb(II)	54.94	0.095	5.219	0.9859	0.521	8.035	1.49	0.9992

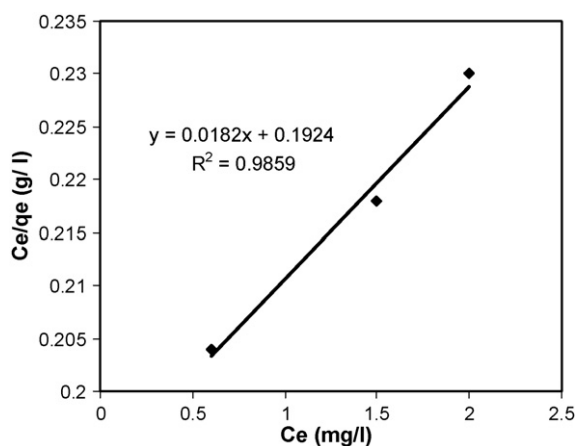


Fig. 3. Langmuir plot for the adsorption of Pb(II) on NOC.

where C_0 is the initial metal ion concentration (mg/l) and b is the Langmuir constant. The value of R_L calculated from different initial concentrations are reported in Table 2. The R_L for Cu(II) and Cd(II) are 0.9015 and 0.4690, respectively. The values are in between 0 and 1 showing favorable adsorption on NOC [27].

Freundlich isotherm is given by equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where K_f and $1/n$ are known as Freundlich constants.

The values of K_f and n were calculated from the intercept and slope of the Freundlich plot (Fig. 4). K_f expresses the adsorption capacity of adsorbent (Table 2). The heterogeneity factor n is a measure of deviation from linearity of the adsorption. The value of $n > 1$ for Pb(II) (Table 2) indicates favorable adsorption by NOC at different concentrations [28]. The higher value of

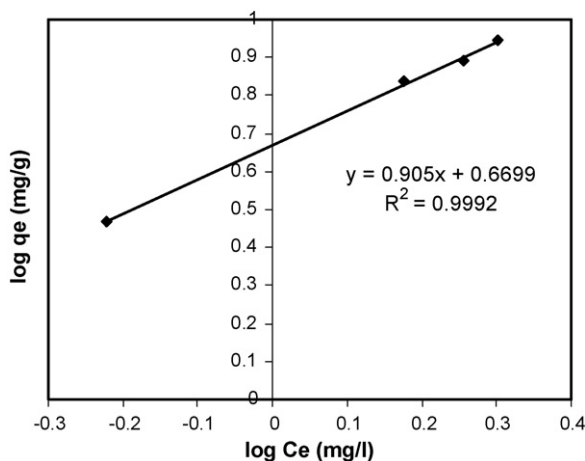


Fig. 4. Freundlich plot for the adsorption of Pb(II) on NOC.

regression coefficient (R^2) in case of Freundlich model indicates better applicability of the model.

3.5. Thermodynamic studies

The thermodynamic parameters such as enthalpy change (ΔH°) and entropy change (ΔS°) were obtained from the Van't Hoff equation.

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

ΔS° and ΔH° were calculated from the slope and intercept of linear plots of $\log K_c$ versus $1/T$ (Fig. 5) for Pb(II). Equilibrium constant (K_c) calculated from the following relation ship [2].

$$K_c = \frac{C_{Ae}}{C_e} \quad (5)$$

where C_{Ae} and C_e are the equilibrium concentration (mg/l) on adsorbent and in solution, respectively. Standard free energy change (ΔG°) was then calculated from the equation.

$$\Delta G^\circ = -RT \ln K_c \quad (6)$$

where T is the absolute temperature and R is the gas constant.

The positive values of ΔH° (Table 3) suggest endothermic nature of adsorption of Pb(II) on NOC. The free energy change (ΔG°) of the process decreases with increase in temperature, which indicated that the process is spontaneous and spontaneity increases with increase in temperature. The positive value of entropy change (ΔS°) shows the increase randomness at the solid/solution interface during the adsorption of Pb(II) on NOC.

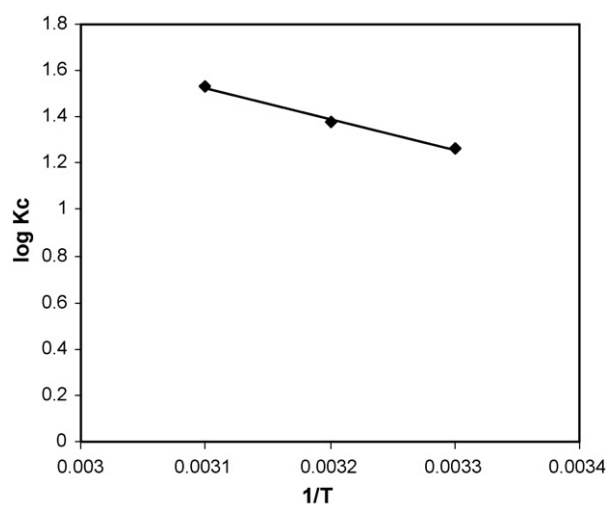


Fig. 5. Plot of $\log K_c$ vs. $1/T$ for Pb(II) on NOC.

Table 3
Thermodynamic parameters for the adsorption of Pb(II) on NOC at different temperatures

Metal ions	Temperature (°C)	K_c	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol)
Pb(II)	30	1.261	−7.277	25.75	0.109
	40	1.38	−8.367		
	50	1.53	−9.457		

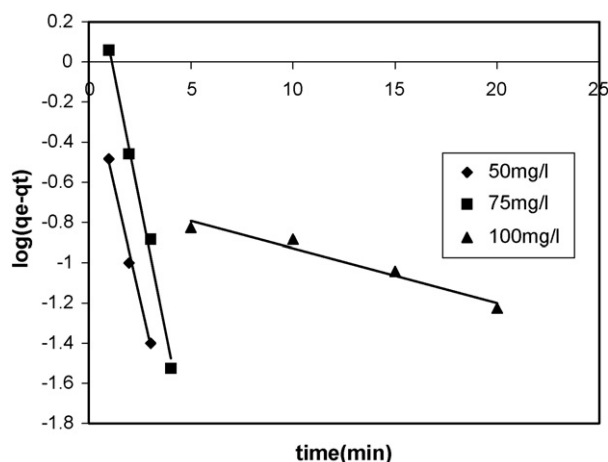


Fig. 6. Pseudo-first-order kinetics for the adsorption of Pb(II) on NOC at different concentrations.

3.6. Kinetics studies

A quantitative understanding of the adsorption is possible with the help of kinetic models. A pseudo-first-order kinetic model as expressed by Lagergren [29] can be written as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} \times t \quad (7)$$

where q_e and q_t are the amount of metal adsorbed (mg/g) at equilibrium and at time t , respectively and K_1 is the pseudo-first-order equilibrium rate constant (l/min). A plot of $\log(q_e - q_t)$ versus t gives straight line and confirms the applicability of the pseudo-first-order rate equation (Fig. 6).

Pseudo-second-order adsorption rate equation may be expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e} \times t \quad (8)$$

where K_2 is the pseudo-second-order adsorption rate constant (g/mg min). A plot of t/q_t versus t produces straight line and indicates the applicability of pseudo-second-order model (Fig. 7).

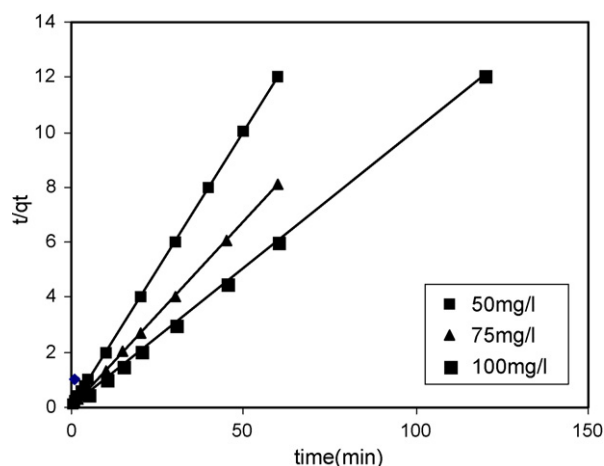


Fig. 7. Pseudo-second-order kinetics for the adsorption of Pb(II) on NOC at different concentrations.

In order to compare quantitatively the applicability of kinetic models in fitting to data, the percent relative deviation (P), given by the following equation was calculated:

$$P = \frac{100}{N} \sum \left\{ \frac{[q_{e(\text{exp})} - q_{e(\text{theo})}]}{q_{e(\text{exp})}} \right\} \quad (9)$$

where $q_{e(\text{exp})}$ is the experimental value of q_e at any value of C_e , $q_{e(\text{theo})}$ the corresponding theoretical value of q_e and N is the number of observations. It is found that lower the value of percentage deviation (P), better is the fit. It is generally accepted that when P value is less than 5, the fit is considered to be excellent [26]. The results have been analyzed using Eqs. (7) and (8). The experimental data fitted well in both the equations. The values of $q_{e(\text{theo})}$ calculated from these models are compared with experimental values $q_{e(\text{exp})}$ in Table 4. It is found that values of $q_{e(\text{theo})}$ calculated from the pseudo-first-order kinetic model differed appreciably from the experimental values $q_{e(\text{exp})}$. The % deviation (P) is also very high. On the other hand, values of $q_{e(\text{theo})}$ are found to be very close to $q_{e(\text{exp})}$ when pseudo-second-order rate equation was applied. The % deviation (P) is well within the range and also the values of correlation coef-

Table 4
Pseudo-first-order and pseudo-second-order kinetic constants for the adsorption of Pb(II) on NOC

Metal ion	Conc. (mg/l)	Pseudo-first-order kinetic					Pseudo-second-order kinetic				
		K_1 (l/min)	$q_{e(\text{theo})}$ (mg/g)	$q_{e(\text{exp})}$ (mg/g)	R^2	P	K_2 (g/mg min)	$q_{e(\text{theo})}$ (mg/g)	$q_{e(\text{exp})}$ (mg/g)	R^2	P
Pb(II)	50	1.055	1.105	4.99	0.9943	77.8	4.715	4.99	4.99	1	0
	75	1.191	3.89	7.42	0.994	47.6	2.082	7.42	7.42	1	0
	100	0.062	0.221	9.94	0.9624	97.8	0.863	9.95	9.94	1	0.1

Table 5

Adsorption and desorption of Cu(II), Cd(II) and Pb(II) in single and multimetal systems on NOC by batch and column process

Metal solutions	Metal	Amount loaded (mg)	Batch process (amount of adsorbent = 0.5 g)		Column operation (amount of adsorbent = 0.5 g)	
			% Adsorption	% Recovery	% Adsorption	% Recovery
Single metal system solution	Cu(II)	2.5	92	36.2	100	100
	Cd(II)	2.5	98	8.2	95.2	95.7
	Pb(II)	2.5	95.7	55.5	88.4	94.1
Multimetal system in DDW	Cu(II)	1.0	90	38.84	100	100
	Cd(II)	1.0	99.5	49.75	99.3	100
	Pb(II)	1.0	99.3	39.61	100	71
Multimetal system in tap water	Cu(II)	1.0	85	23.5	100	99
	Cd(II)	1.0	96.3	48.1	99.8	91.6
	Pb(II)	1.0	99.5	64.8	100	83

ficients (R^2) are very high as compared to pseudo-first-order rate model. It is therefore confirmed that adsorption of Pb(II) followed pseudo-second-order rate equation.

3.7. Removal and recovery

In order to explore the practical utility of the adsorbent, removal and recovery of Cu(II), Cd(II) and Pb(II) was carried out by batch and column processes using single metal system, multimetal system in DDW and multimetal system prepared in tap water since wastewater contains other ions also similar to tap water (like Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , Cl^- , etc.) and results are compared in Table 5. It is found that in single metal system adsorption of Cu(II) by column process is higher than batch process, adsorption of Cd(II) is comparable when batch and column processes are used while adsorption of Pb(II) is higher by batch process. The removal of Cu(II), Cd(II) and Pb(II) by batch or column process is not very much affected when multimetal system in DDW and tap water are used, showing that removal efficiency of these metals remains the same even in the presence of other ions present in tap water. However, the recovery of Cu(II), Cd(II) and Pb(II) is poor by batch process (Table 5) as compared to column process. The % recovery of Pb(II) is slightly decreased in multimetal system in DDW (Pb(II) = 71%) and tap water (Pb(II) = 83%). Elution of Cd(II), Pb(II) and Cu(II) in multimetal systems in DDW and tap water from NOC are shown in Figs. 8 and 9. It is important to note that maximum elution of all the metals occur with in 10 ml fraction of the effluent, showing that metal ions can be preconcentrated effectively using NOC as adsorbent.

The amount of adsorbent required for complete removal of heavy metal ions can be found out by determining the breakthrough capacity. The breakthrough capacities of Cu(II), Cd(II) and Pb(II) are found to be 10, 15 and 30 mg/g (Figs. 10–12). When column became saturated with metal ions (or exhausted), the desorption studies were carried out by passing 0.1 M HCl solution through each column. Fig. 13 indicates that 2.5, 2.485, 1.6 and 0 mg of Cu(II) was adsorbed consecutively from each 50 ml fraction of Cu(II) (50 mg/l) when passed through the column. This indicates that total 6.58 mg of Cu(II) was adsorbed from 200 ml of Cu(II) solution before the column exhausted.

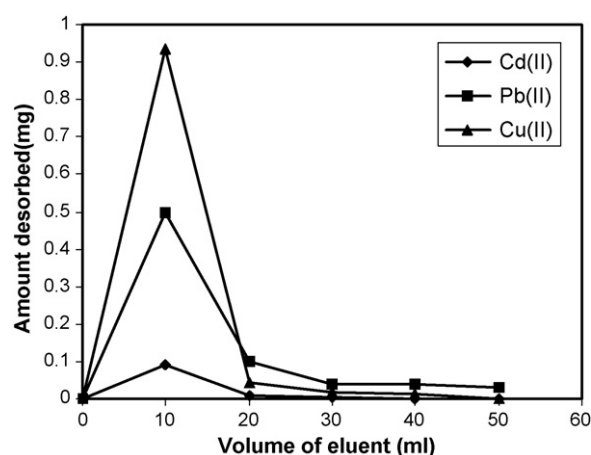


Fig. 8. Desorption studies of a mixture of Cd, Pb and Cu in DDW by column using 0.1 M HCl as an eluent.

0.1 M HCl solution was then passed through this column. Eight fractions of 10 ml each were collected consecutively. The Cu(II) recovered from 80 ml effluent was 6.71 mg (100% recovery of Cu(II)). Similarly Fig. 14 indicates that 2.5, 2.5, 2.5, 2.5, 2.5, 2.5, 2.05, 1.45 and 0.9 mg of Pb(II) was adsorbed conse-

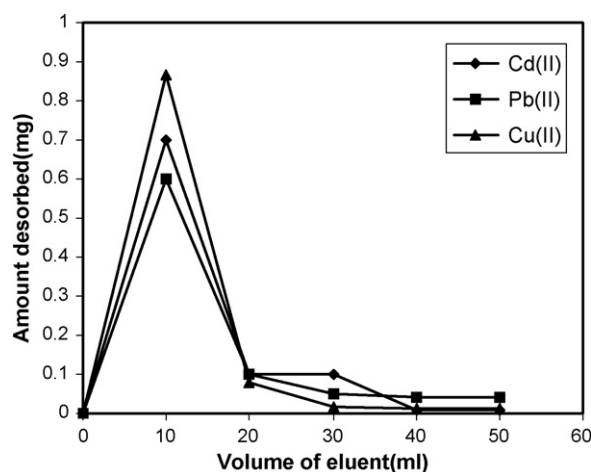


Fig. 9. Desorption studies of a mixture of Cd, Pb and Cu in tap water by column using 0.1 M HCl as an eluent.

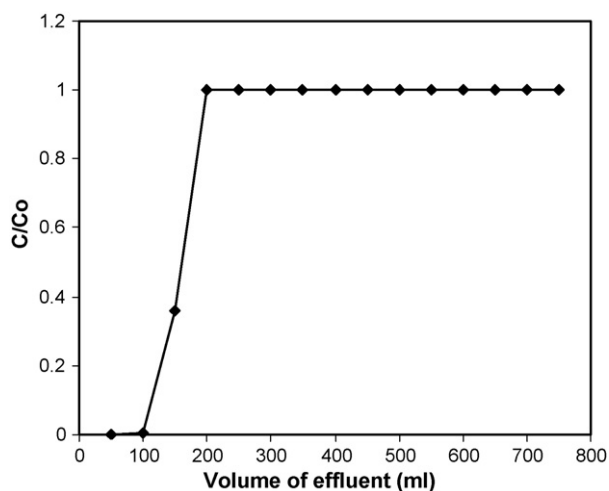


Fig. 10. Breakthrough capacity curve for the adsorption of Cu(II) on NOC.

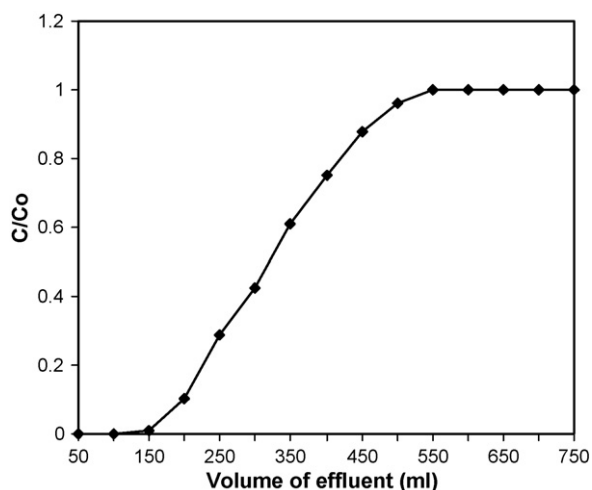


Fig. 11. Breakthrough capacity curve for the adsorption of Cd(II) on NOC.

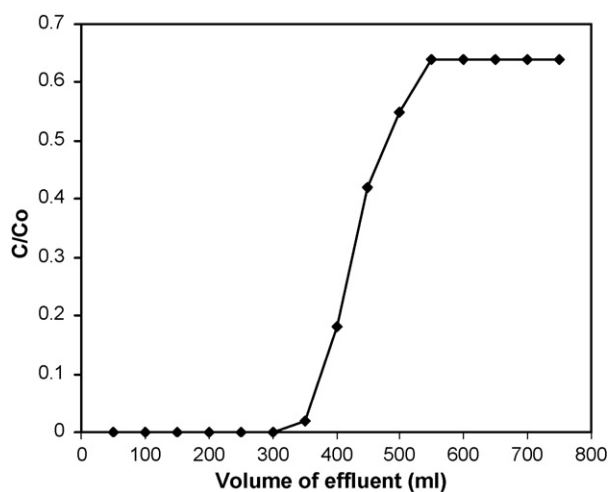


Fig. 12. Breakthrough capacity curve for the adsorption of Pb(II) on NOC.

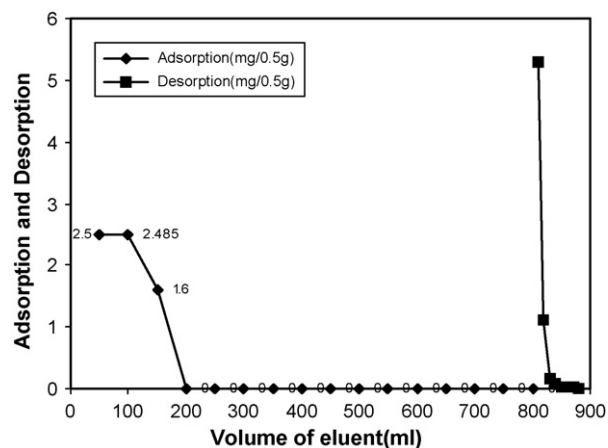


Fig. 13. Adsorption and desorption of Cu(II) on NOC by column process.

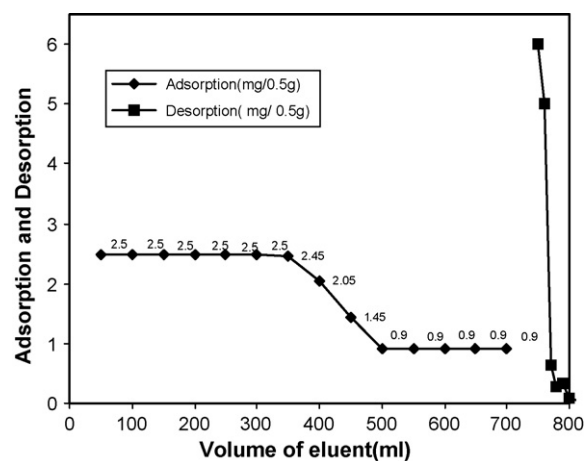


Fig. 14. Adsorption and desorption of Pb(II) on NOC by column process.

cultively from each 50 ml fraction of Pb(II) solution before the column exhausted. This indicates that 21.85 mg of Pb(II) was adsorbed from 500 ml of Pb(II) solution. 0.1 M HCl solution was passed through this column. Eight fractions of 10 ml each were collected consecutively. The Pb(II) recovered from 80 ml effluent was 12.44 mg (57% recovery of Pb(II)).

It can be inferred from above findings that waste water containing small quantities of Cu(II), Cd(II) and Pb(II) can be treated effectively using NOC as adsorbent. The column operation is more effective because spent or exhausted adsorbent can be regenerated easily by 0.1 M HCl and at the same time these metal ions can be recovered in small volume of effluent. This may help in easy disposal of extracted/preconcentrated metal solution.

4. Conclusion

Neem oil cake (NOC) is used as bio-pesticide and bio-fertilizer in organic farming. The advantage of using NOC as biosorbent is that its decomposition is fast as compared to other bulky organic sorbents because of its low C/N ratio. NOC is highly selective for Pb(II) and shows 98% adsorption of Pb(II) at pH 4. The adsorption studies indicate that Freundlich model is better obeyed. Thermodynamic parameters (ΔH° and ΔG°)

suggest that adsorption process is endothermic and spontaneous. The kinetics data are best fitted in second order rate equation as evident from the values of % deviation (P) and regression coefficients (R^2). The breakthrough capacities for Cu(II), Cd(II) and Pb(II) are found to be 10, 15 and 30 mg/g, respectively. The analytical applications could be demonstrated by using NOC for the removal and recovery of Cu(II), Cd(II) and Pb(II) from single and multimetal solution systems. It has been found that removal and recovery of Cu(II), Cd(II) and Pb(II) is better by column operation as compared to batch process in single metal and multimetal systems. The maximum efficiency of NOC has been demonstrated by eluting Cu(II) and Pb(II) from exhausted columns (i.e. beyond exhaustive capacity) and it has been found that 100% Cu(II) could be recovered while recovery of Pb(II) is 57% when 0.1 M HCl was used as eluent. NOC therefore is an effective biosorbent and can be utilized for the removal and recovery of Cu(II), Cd(II) and Pb(II) from water and wastewater. The regeneration of the adsorbent and maximum recovery of these ions in small volume of effluent makes the adsorbent more economical and easy disposal of the preconcentrated metal ions.

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References

- [1] UNEP, United Nations Environmental Programme, Industrial and Environment Office, Paris, 1989.
- [2] C. Namasivayam, K. Ranganathan, Water Res. 29 (1995) 1737–1744.
- [3] K. Vijayarghavan, J. Jegann, K. Palanivelu, M. Velan, Chem. Eng. J. 106 (2) (2005) 177–184.
- [4] B. Volesky, Hydrometallurgy 59 (2/3) (2001) 203–216.
- [5] E.W. Wilde, J.R. Benemann, Biotechnol. Adv. 11 (1993) 781.
- [6] B. Volesky, Z.R. Holan, Biotechnol. Prog. 11 (1995) 235.
- [7] B. Volesky, I. Prasetyo, Biotech. Bioeng. 47 (1994) 1010–1015.
- [8] S.F. Al-Asheh, R. Banat, Z. Al-Omari, Duvnjak, Chemosphere 41 (2000) 659.
- [9] Y. Sag, B. Akcael, T. Kutsal, Process Biochem. 37 (2001) 35.
- [10] K.H. Chong, B. Volesky, Biotechnol. Bioeng. 47 (1995) 451.
- [11] Z. Aksu, U. Acikel, Process Biochem. 34 (1999) 589.
- [12] S. Singh, B.N. Rai, L.C. Rai, Process Biochem. 36 (2001) 1205.
- [13] Z.R. Holan, B. Volesky, I. Prasetyo, Biotechnol. Bioeng. 41 (1993) 819.
- [14] F. Pagnanelli, M. Trifoni, F. Becolchini, A. Esposito, L. Toro, F. Veglio, Process Biochem. 37 (2001) 115.
- [15] M. Loaec, R. Olier, J. Guezennec, Water Res. 31 (1997) 1171.
- [16] A. Saeed, M. Iqbal, M.W. Akhtar, J. Hazard. Mater. B 117 (2005) 65–73.
- [17] Evaluation of Cold-Pressed Oil from the Seed Kernels of *Azadirachta indica* (A.Juss), Meliaceae (Neem) for use in Listable Therapeutic Goods, Office of Complementary Medicines, Therapeutic Goods Administration (TGA), Australia.
- [18] A.C. Gaur, S. Neelakanta, K.S. Dargan, Organic Manures, Indian Council of Agricultural Research, New Delhi, 1981, pp. 68–69.
- [19] Z. Aksu, D. Akpınar, Separ. Purif. Technol. 21 (2001) 87.
- [20] E. Luef, T. Prey, C.P. Kubicek, Appl. Microbiol. Biotechnol. 34 (1991) 688.
- [21] K.S. Low, C.K. Lee, K.P. Lee, Bioresource Technol. 44 (1993) 109.
- [22] I. Aldov, E. Fourest, B. Volesky, Can. J. Chem. Eng. 73 (1995) 516.
- [23] A. Saeed, M. Iqbal, M.W. Akhtar, Pak. J. Sci. Ind. Res. 45 (2002) 206.
- [24] J.S. Chang, R. Law, C.C. Chang, Water Res. 31 (1997) 1651.
- [25] D.C. Sharma, C.F. Foster, Water Res. 27 (7) (1993) 1201–1208.
- [26] E. Ayranci, O. Duman, J. Hazard. Mater. B 124 (2005) 125–132.
- [27] V.J.P. Poots, G. Mc Kay, J.J. Healy, Water Pollut. Control. Fed. J. 50 (1978) 926.
- [28] A. Ozcan, A.S. Ozcan, S. Tunali, T. Akar, I. Kiran, J. Hazard. Mater. B 124 (2005) 200–208.
- [29] M. Ajmal, R.A.K. Rao, R. Ahmad, J. Ahmad, J. Hazard. Mater. B 87 (2001) 127–137.
- [30] H. Schmutterer (Ed.), The Neem Tree: Source of Unique Natural Products for Integrated Pest Management, Medicine, Industry and Other Purposes (Hardcover), 2nd ed., VCH Verlagsgesellschaft, Weinheim, Germany, 2002.