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Biosorption of bivalent metal ions from aqueous solution by an agricultural waste: Kinetics, thermodynamics and environmental effects

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 ability of Neem oil cake (NOC), a bio-waste material to remove Cu(II) and Cd(II) ions from aqueous solution was investigated. The influence of pH, sorbent dose, concentration, temperature, and contact time on the sorption of Cu(II) and Cd(II) on NOC has been studied by batch process. The sorption was found to be maximum in acidic medium and increases with increase in initial concentration. Percent deviation (P) and regression coefficient (r^2) for Langmuir and Freundlich sorption isotherms shows better fitting of the models. Thermodynamics parameters indicate that the process is endothermic and spontaneous. Activation energies for Cu(II) and Cd(II) were calculated from Dubinin–Redushkevich (D–R) isotherms are high 8.3–8.7 and 7.17–11.4 kJ mol^{−1} showing that chemisorption is involved. The sorption kinetics was found to follow pseudo-second-order model.

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1. Introduction

Toxicities of water bodies through the discharge of industrial effluents are a world wide environmental problem. Industrial wastewater often contains considerable amount of heavy metals and organic pollutants that would endanger public health and the environment if discharged without adequate treatment. The heavy metals are of special concern because they are non-degradable and therefore persistent [1].

Copper (Cu(II)) and Cadmium (Cd(II)) are toxic heavy metals normally found in industrial wastewater. Cd(II) is more toxic of the two. It makes its way to water bodies through wastewater from metal plating industries, industries of Cd–Ni batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys [2]. Cu(II) in low concentration (<5 mg L^{−1}) is generally considered to be toxic for man [3]. Industries discharging Cu(II) 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 [4,5]. Poisoning of Cd(II) in humans causes high blood pressure, kidney damage and destruction of testicular tissue and Red blood cells (RBCs) [6]. In small amounts Cd(II) is associated with hypertensive diseases [7] and is considered as carcinogenic to man [8]. The permissible limits of Cd(II) is 0.05 mg L^{−1} [2]. While, Cu(II) causes gastrointesti-

nal catarrh, cramps in calves, hemochromatosis (characterized by bronzed skin, enlarged liver, abnormalities of pancreas and joints) and skin dermatitis brasschills, usually accompanied by high fever [9,10]. The permissible limit of Cu(II) for drinking water following WHO's guidelines is 1 mg L^{−1} [11].

Many chemical methods such as chemical precipitation, electro floatation, ion-exchange and reverse osmosis have been used for the removal of heavy metals. However, these processes are economically non-feasible especially in developing countries. The sorption process has been found to be economically appealing for the removal of heavy metals with better removal efficiency from wastewater.

Activated carbon (AC) is a common conventional adsorbent used to sequester heavy metals from wastewater but it is expensive due to the regeneration cost and loses in the application process [12]. Several sorbents have been used earlier for the treatment of Cu(II) and Cd(II) rich effluents [13–23]. The sorption behavior of orange fruit peel, saw dust, pyrolusite, kyanite, rice husk and *Parthenium hysterophorus* for the removal and recovery of Ni(II), Cr(VI), Pb(II), Cu(II) and Cd(II) from rivers and industrial wastewater have been studied in our laboratory [24–28].

Mustard oil cake (MOC) studied earlier in our laboratory was found to be excellent sorbent for the removal of Cu(II) from wastewater [3]. This has encouraged us to explore the sorption properties of Cu(II) and Cd(II) by Neem oil cake (NOC), a bio-waste material obtained as byproduct of Neem fruit. The composition of NOC shows N₂ – 5.2%, P₂O₅ – 1%, K₂O – 1.4% [29]. Oil cakes in general have low C/N ratio therefore their degradation is rapid [29].

* Corresponding author. Tel.: +91 571 2700920x3000.
E-mail address: rakrao2000@yahoo.com (R.A.K. Rao).

This is an additional advantage that spent oil cakes are degraded rapidly and hence their disposal is easy in comparison to other biosorbents.

Neem (*Azadirachta indica*) is a fast growing, usually evergreen plant, which reaches a height of 15–20 m and a trunk girth of 1.5–3.5 m. Neem has been widely explored for solving various problems related to agriculture, public health, population control and environmental pollution [30]. The main components in Neem are azadirachtin, salannin, nimbin and nimbidin. Other important constituents are a number of fatty acids like oleic acid, stearic acid, palmitic and linoleic acids, etc. [31]. The presence of OH and COOH functional groups may be responsible for the sorption of metal ions on NOC. Neem has been recognized as a natural air purifier and it has been suggested that the planting of Neem trees on roadside is an effective way to regulate traffic related pollution [32].

2. Materials and methods

2.1. Sorbent

Oil is extracted from the fruit of Neem (*A. indica*) and waste matter left after extraction is known as Neem oil cake. 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 sorbent was sieved to 300–100 µm particle size and used as such.

2.2. Sorbate solution

Stock solutions of Cu(II) and Cd(II) were prepared (1000 mg L⁻¹) by dissolving the desired quantity of their nitrate salts (A.R. grade) in DDW.

2.3. Sorption studies

Sorption studies were carried out by batch process. 0.5 g sorbent was placed in a conical flask with 50 mL solution of metal ions of desired concentration. The mixture was shaken in temperature controlled shaker incubator for 2 h at 120 rpm. The mixture was then filtered using Whatman filter paper No. 41 and final concentration of metal ion was determined in the filtrate by atomic absorption spectrometry (AAS) (GBC 902). The amount of metal ions sorbed was calculated by subtracting final concentration from initial concentration.

2.4. Effect of pH

The effect of pH on the sorption of Cu(II) and Cd(II) was studied by batch process as follows: 100 mL of metal solution was taken in beaker. The desired pH of solution was adjusted by adding dilute solution of 0.1 M HCl and 0.1 M NaOH. The concentration of metal ions in this solution was then determined (initial concentration). Fifty millilitres of this solution was taken in a conical flask and was treated with 0.5 g sorbent and after equilibrium, the final concentration of metal ions was determined. Since adjusted pH of the sorbate changes when equilibrium is reached therefore final pH at equilibrium was also recorded. The difference in final pH_f and initial pH_i ($\Delta H = \text{pH}_f - \text{pH}_i$) was found to be 4.1, 2.5, 0.9 and -3.2 for Cu(II) and 3.9, 2.6, 1.4 and -3.1 for Cd(II), respectively.

2.5. Effect of contact time

A series of 250 mL conical flasks, each having 0.5 g sorbent and 50 mL solution (of known metal concentration) were shaken in

temperature controlled shaker incubator at 120 rpm and at the pre-determined time intervals (0.5, 1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 60, 80, 100 and 120 min) the solution of the specified flask was taken out and filtered. The concentration of metal in the filtrate was determined by AAS. The amount of metal sorbed in each case was then determined as described earlier.

2.6. Effect of sorbent dose

A series of 250 mL conical flasks each containing 50 mL of metal solution (50 mg L⁻¹) were treated at different temperatures by varying the amount of sorbent (0.1–0.8 g). The flasks were shaken in temperature controlled shaker incubator at 120 rpm and after equilibrium (24 h) the solutions were filtered. The amount of metal ions in filtrate was then determined by AAS. The amount of metal sorbed in each case was calculated as above.

2.7. Quality assurance and quality control

To make sure that no metal ions were released to the solution from the sorbent, an equilibrium test was performed using sorbent (NOC) in DDW. For assuring quality in the sorption 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. The percent relative standard deviation (R.S.D.) for samples was calculated and if the value of percent R.S.D. for any sample was greater than 10% the data were declared unusable.

3. Result and discussions

3.1. Effect of concentration

The increase in initial concentration of Cu(II) and Cd(II) ions results in an increase in the sorption capacity, q_e (mg g⁻¹). This is a usual phenomena observed on various sorbents since transfer of metal ions from bulk to the surface of the sorbent increases with increase in concentration of metal ions. This is the basic property of the sorbent to be utilized for the removal of metal ions from wastewater. However, in many cases where natural sorbents are used, it fails to give reproducible results. The reasons are many like non-uniform particle size and surface properties, etc. Therefore an extensive study for the sorption of Cu(II) and Cd(II) has been carried out. The data in Table 1 shows that sorption capacity of Cu(II) and Cd(II) increases with increase in initial concentrations. The standard deviation in each case is well within the range. These data indicate the reproducibility of the results.

3.2. Effect of pH

The percentage sorption of Cu(II) and Cd(II) on NOC increases with increase in pH, attaining maximum at pH 4.4 and 4.5 for Cu(II) and Cd(II) respectively (Fig. 1). Availability of negatively charged groups on the sorbent surface is necessary for the sorption of metals [3]. Sorption at pH 2 is less as the sorbent surface is potentially changed due to the presence of H⁺ and H₃O⁺. In such system H⁺ compete with metal ions [33] resulting in active sites to become protonated to the virtual exclusion of metal binding on the sorbent surface [34]. This means that at higher H⁺ concentration, the sorbent surface becomes more positively charged thus reducing the attraction between sorbent and metal cations [35]. In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake and therefore metal sorption tends to increase significantly by increasing pH. Thus,

Table 1
Effect of initial concentration on sorption capacity of Cu(II) and Cd(II) on NOC (Reproducibility test)

Initial concentration C_0 (mg L ⁻¹)	Cu(II)					Cd(II)				
	Average final concentration C_e (mg L ⁻¹)	Average sorption capacity q_e (mg g ⁻¹)	Standard deviation of q_e	Relative standard deviation of q_e	Average final concentration C_e (mg L ⁻¹)	Average sorption capacity q_e (mg g ⁻¹)	Standard deviation of q_e	Relative standard deviation of q_e	Average final concentration C_e (mg L ⁻¹)	Average sorption capacity q_e (mg g ⁻¹)
10	0.167	0.983	0.004	0.478	0.267	0.973	0.000	0.059	0.267	0.973
20	0.600	1.940	0.010	0.515	0.320	1.968	0.001	0.050	0.320	1.968
30	1.267	2.873	0.011	0.400	0.650	2.935	0.001	0.034	0.650	2.935
40	1.967	3.803	0.015	0.402	0.800	3.920	0.000	0.000	0.800	3.920
60	4.567	5.543	0.015	0.276	1.630	5.836	0.000	0.000	1.630	5.836
70	5.033	6.496	0.005	0.089	4.200	6.580	0.010	0.119	4.200	6.580
80	6.100	7.390	0.010	0.130	3.030	7.697	0.011	0.150	3.030	7.697
90	12.00	7.800	0.010	0.128	6.500	8.350	0.010	0.119	6.500	8.350
100	13.100	8.690	0.010	0.115	6.500	9.350	0.017	0.185	6.500	9.350

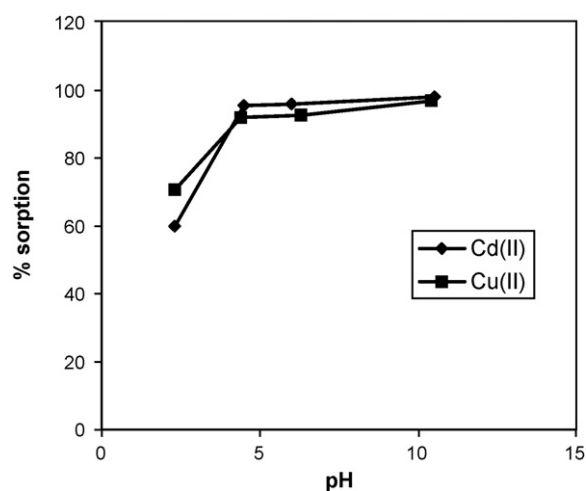


Fig. 1. Effect of pH on the sorption of Cu(II) and Cd(II) on NOC.

50 mg L⁻¹ solutions of Cu(II) and Cd(II) at pH values 4.4 and 4.5 shows 92 and 95.3% sorption, respectively.

3.3. Effect of contact time

Sorption of Cu(II) and Cd(II) on NOC at various initial concentrations was carried at different intervals of time (5–60 min). The maximum uptake of Cu(II) was found to be 2.32, 4.91 and 7.2 mg g⁻¹ at 25, 50 and 75 mg L⁻¹ initial Cu(II) concentrations respectively. The extent of sorption increased rapidly in the initial stages and then became slow at later stages till the equilibrium is attained. Equilibrium time for the sorption of Cu(II) at different concentrations was found to be 30 min showing that equilibrium time is independent of initial concentration of Cu(II) (Fig. 2). Similarly sorption of Cd(II) increases with increase in initial concentration (Fig. 3). The maximum sorption capacities at equilibrium were found to be 1.47, 2.4 and 4.94 mg g⁻¹ at 15, 25 and 50 mg L⁻¹ initial Cd(II) concentration, respectively. The equilibrium time was found to be 10, 50 and 60 min, respectively, for the initial Cd(II) concentrations of 15, 25 and 50 mg L⁻¹ showing that equilibrium time depends upon the initial Cd(II) concentrations.

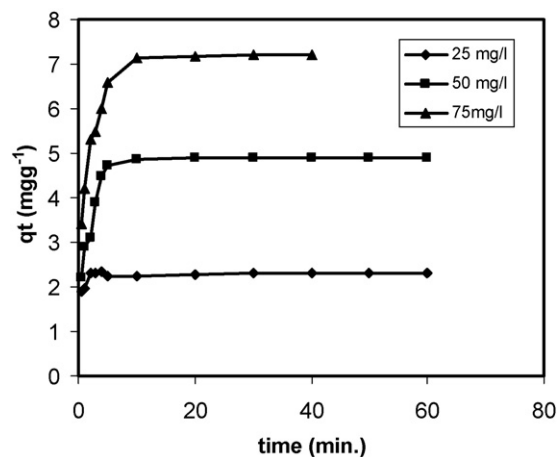


Fig. 2. Effect of time on the sorption of Cu(II) on NOC.

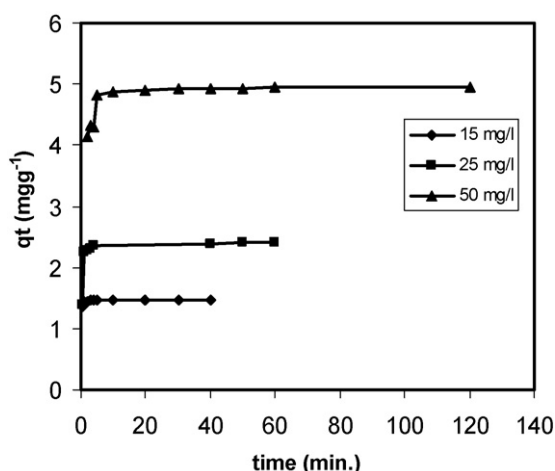


Fig. 3. Effect of time on the sorption Cd(II) on NOC.

3.4. Effect of sorbent doses

The sorption density (mg g^{-1}) and percentage (%) sorption of Cu(II) and Cd(II) by varying the dose of NOC at different temperatures are shown in Figs. 4 and 5. The %sorption increases while sorption density decreases as the sorbent dose is increased. An increase in temperature also increases the %sorption. It may be concluded that by increasing the sorbent dose, the removal efficiency of NOC increases. The decrease in sorption capacity may be due to the fact that some sorption sites may remain unsaturated during the sorption process where as the number of sites available for sorption increases by increasing the sorbent doses [36].

3.5. Sorption isotherms

Sorption data for wide range of adsorbate concentration are most conveniently described by sorption isotherms, such as the Langmuir and Freundlich isotherms.

The Langmuir equation is:

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

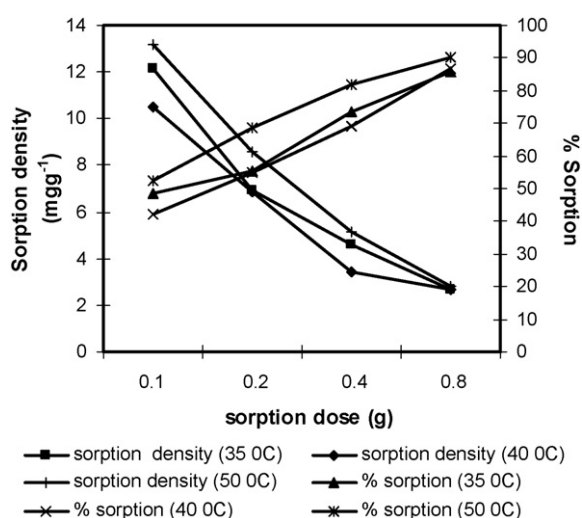


Fig. 4. Effect of sorbent dose on %sorption and sorption density of Cu(II) at different temperatures (pH 4.5).

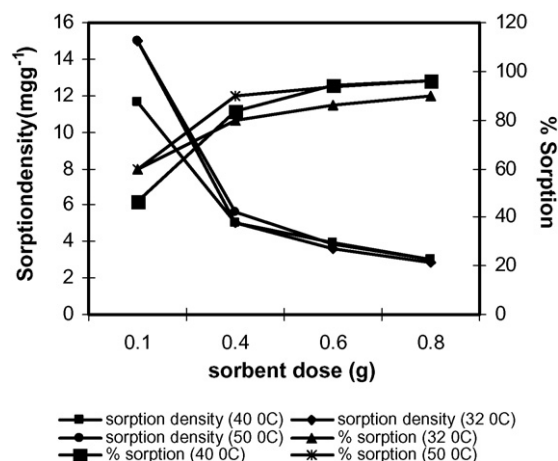


Fig. 5. Effect of sorbent dose on %sorption and sorption density of Cd(II) at different temperatures.

where C_e is the equilibrium concentration of sorbate (mg L^{-1}), q_e is the sorption capacity (mg g^{-1}), b (L g^{-1}) and q_m (mg g^{-1}) are 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 vs. C_e . The coefficient b in Langmuir equation is related to the binding energy with a pH-dependent equilibrium constant. q_m is the maximum sorption capacity determined by the number of reactive surface sites in an ideal monolayer system. q_m is calculated for various sorbents used for the removal of Cu(II) and Cd(II) and compared with the present study (Table 2).

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

$$R_L = \frac{1}{1 + bC_0} \quad (2)$$

where C_0 is the initial metal ion concentration (mg L^{-1}) and b the Langmuir constant. The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [37]. It is found that sorption of Cu(II) and Cd(II) on NOC is favorable (Table 3).

Freundlich isotherm is given by equation:

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

where K_f and n are Freundlich constants.

The values of K_f and n were calculated from the intercept and slope of the Freundlich plots are shown in Table 3. K_f indicates the sorption capacity of adsorbent. The constant n is a measure of deviation from linearity of the sorption. The values of n is not only a measure of the deviation from linearity, but informs about the het-

Table 2
Sorption capacities (mg g^{-1}) of various sorbents for Cu(II) and Cd(II)

Sorbents	Cu(II)	Cd(II)	Reference
Date pits	–	6.50	[43]
Chitosan	16.80	8.54	[44]
Clinoptilolite	1.64	2.40	[45]
Montmorillonite	–	0.72	[46]
Flyash–wollastonite	1.18	–	[47]
Tannic acid modified activated carbon	2.73	2.46	[48]
Oligotrophic peat	6.41	–	[49]
Bentonite	–	11.41	[47]
Chabazite	5.10	6.70	[50]
NOC	9.398	11.82	[Present study]

Table 3
Langmuir and Freundlich constants for the sorption of Cu(II) and Cd(II) on NOC

Metal ions	Langmuir constants						Freundlich constants			
	q_m (mg g ⁻¹)	b (L mg ⁻¹)	bq_m (L g ⁻¹)	r^2	R_L	P	K_f (mg g ⁻¹)	n	r^2	P
Cu(II)	9.398	0.4063	3.818	0.9905	0.9015	0.26	2.45	1.92	0.9932	4.8
Cd(II)	11.82	0.0123	6.868	0.9963	0.469	5.8	3.45	2.05	0.9936	0.05

erogeneity degree of the sorption sites. As n approaches zero, the surface site heterogeneity increase. The values of $n > 1$ for Cu(II) and Cd(II) indicate favorable sorption of Cu(II) and Cd(II) by NOC at different concentrations [38].

In order to compare quantitatively the applicability of different models (Langmuir, Freundlich and kinetics models) in fitting to data, the percent relative deviation (P), given by the following equation was calculated

$$P = \frac{100}{N \sum \{|q_{e(\text{exp})} - q_{e(\text{theo})}|/q_{e(\text{exp})}\}} \quad (4)$$

where $q_{e(\text{exp})}$ is the experimental value of q_e at any value of C_e , $q_{e(\text{theo})}$ is 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 [39]. The values of P for Langmuir and Freundlich plots of Cu(II) and Cd(II) indicate that both the models are better obeyed which is also evident from regression coefficient values (Table 3).

3.6. Thermodynamics studies

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

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (5)$$

where, ΔS° and ΔH° were calculated from the slope and intercept of linear plots of $\log K_c$ vs. $1/T$ (Fig. 6) for Cu(II) and Cd(II). Equilibrium constant (K_c) was calculated from the following relationship [1].

$$K_c = \frac{C_{Ae}}{C_e} \quad (6)$$

where C_{Ae} and C_e are the equilibrium concentrations of metal (mg L⁻¹) on sorbent and in solution, respectively.

Free energy change (ΔG°) was calculated from the relation

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

where T (K) is the absolute temperature, R (J K⁻¹ mol⁻¹) gas constant, ΔG° is the standard free energy change.

The positive values of ΔH° for Cu(II) and Cd(II) (Table 4) suggest endothermic nature of sorption. The increase in sorption of Cu(II) and Cd(II) with temperature might have been due to change in the pore size and enhanced rate of intra-particle diffusion [40]. The free energy change (ΔG°) of the process decreases with increase in temperature, which indicates that the process is spontaneous and spontaneity increases with increase in temperature. The positive

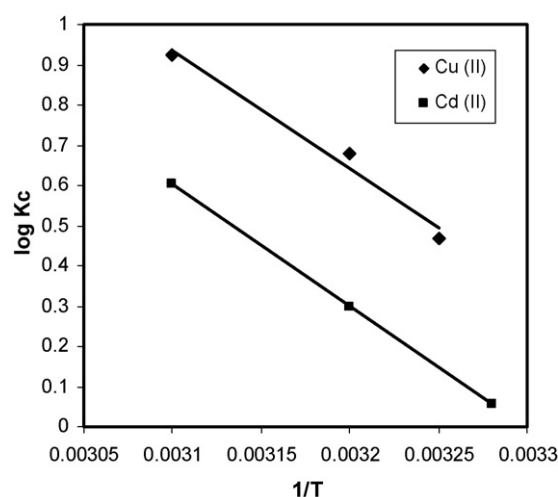


Fig. 6. Plots of $\log K_c$ vs. $1/T$ for Cu(II) and Cd(II).

value of entropy change (ΔS°) shows the increase in randomness at the solid/solution interface during the sorption of Cu(II) and Cd(II).

To distinguish between the physical and chemical sorption on NOC, Dubinin–Redushkevich (D–R) isotherm based on the heterogeneous nature of the sorbent surface is applied. The linear form of (D–R) isotherm equation is [41,42]

$$\ln q_e = \ln q_m - \beta E^2 \quad (8)$$

where β is the activity coefficient constant (mol² J⁻²), q_m the maximum sorption capacity (mol g⁻¹), q_e the sorption capacity (mol g⁻¹), and E the Polanyi potential.

The value of E can be calculated from the relation

$$E = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (9)$$

where T is the absolute temperature (K), R the gas constant (J mol⁻¹ K⁻¹) and C_e the concentration at equilibrium (mol L⁻¹). Hence, by plotting $\ln q_e$ vs. E^2 , the values of q_m from the intercept and β from the slope are generated (Figs. 7 and 8).

The constant β gives an idea about the mean free energy (E_a) (kJ mol⁻¹) of sorption molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship [42].

$$E_a = \frac{1}{(-2\beta)^{1/2}} \quad (10)$$

Table 4
Thermodynamic parameters for the sorption of Cu(II) and Cd(II) on NOC at different temperatures

Metal ions	Temperature (°C)	K_c	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)
Cu(II)	35	0.469	-3.07	56.374	0.193	8.7
	40	0.678	-4.035			8.9
	50	0.923	-5.965			8.3
Cd(II)	32	0.057	-0.28	57.975	0.191	9.8
	40	0.299	-1.808			11.4
	50	0.602	-5.319			7.17

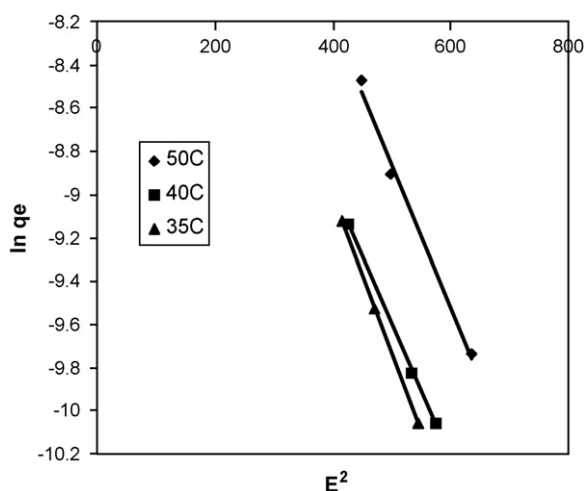


Fig. 7. D-R isotherm of Cu(II).

The magnitude of E_a for the sorption of Cu(II) and Cd(II) on NOC lies between 8.3–8.7 and 7.17–11.4 kJ mol⁻¹, respectively, indicating that the sorption process is chemical in nature.

3.7. Kinetics of sorption

A quantitative understanding of the sorption is possible with the help of kinetic models. The pseudo-first-order kinetic model as expressed by Lagergren [28] can be written as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} \times t \quad (11)$$

where q_e and q_t are the amount of metal sorbed (mg g⁻¹) at equilibrium and at time t , respectively, and K_1 is the pseudo-first-order equilibrium rate constant (min⁻¹). A plot of $\log(q_e - q_t)$ vs. t gives straight line confirming the applicability of the pseudo-first-order rate equation (Figs. 9 and 10).

Pseudo-second-order sorption rate equation may be expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e} \times t \quad (12)$$

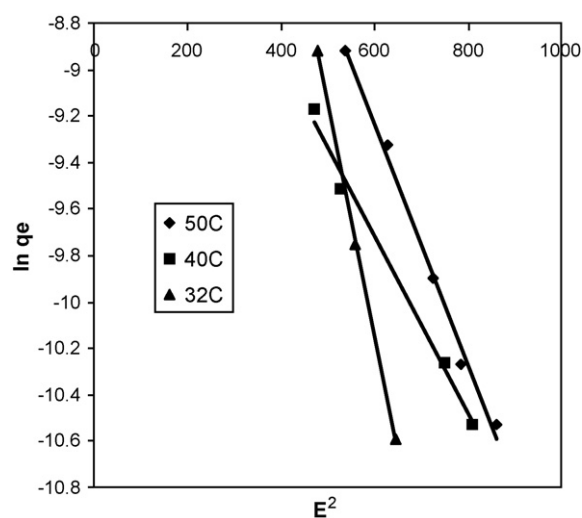


Fig. 8. D-R isotherm of Cd(II).

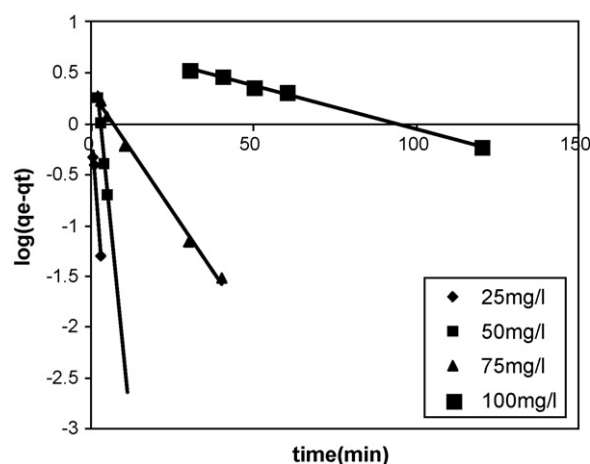


Fig. 9. Pseudo-first-order kinetics for the sorption of Cu(II) on NOC.

K_2 is the pseudo-second-order sorption rate constant (g mg⁻¹ min⁻¹). Straight line plot of t/q_t vs. t indicates the applicability of pseudo-second-order model (Figs. 11 and 12).

The results have been analyzed using Eqs. (11) and (12). The experimental data fitted well in both the equations. The values of $q_{e(\text{theo})}$ calculated from these models are compared with experi-

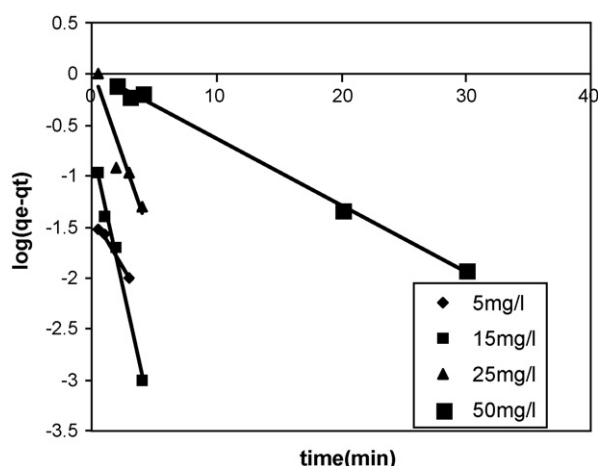


Fig. 10. Pseudo-first-order kinetics for the sorption of Cd(II) on NOC.

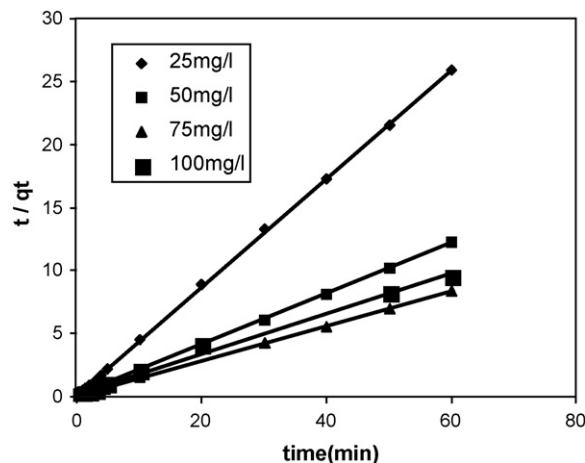
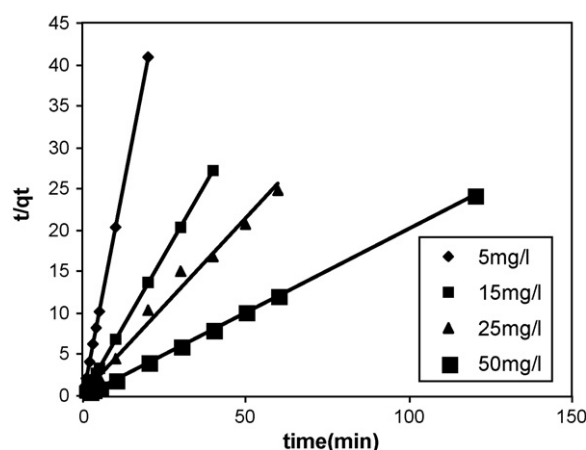


Fig. 11. Pseudo-second-order kinetics for the sorption of Cu(II) on NOC.

Metal ions	Concentration (mg L ⁻¹)	Pseudo-first-order kinetic			Pseudo-second-order kinetic						
		K ₁ (min ⁻¹)	q _{e(theo)} (mg g ⁻¹)	q _{e(exp)} (mg g ⁻¹)	r ²	P	K ₂ (g mg ⁻¹ min ⁻¹)	q _{e(theo)} (mg g ⁻¹)	q _{e(exp)} (mg g ⁻¹)	r ²	P
Cu(II)	25	0.9373	0.86	2.37	0.9843	63.7	2.26	2.32	2.37	0.9998	2.1
	50	0.7512	8.62	4.91	0.9941	75.6	0.343	4.97	4.91	0.9998	1.32
	75	0.1098	2.14	7.2	0.9947	70.3	0.162	7.3	7.2	0.9999	1.39
	100	0.0196	6.35	8.4	0.9959	24.4	0.1225	6.26	8.4	0.9923	25.5
Cd(II)	5	0.456	0.039	0.49	0.9895	91	50.24	0.49	0.49	1	0
	15	1.296	0.196	1.47	0.9841	86.7	39.2	1.47	1.47	1	0
	25	0.818	1.121	2.41	0.9005	53.5	0.469	2.38	2.41	0.9907	1.24
	50	0.151	1.062	4.95	0.9976	78.5	0.568	4.97	4.95	1	0.56



mental values $q_{e(\text{exp})}$ (Table 5). It is found that for pseudo-first-order kinetic model the values of $q_{e(\text{theo})}$ and $q_{e(\text{exp})}$ differed appreciably. The percent deviation (P) values for pseudo-first-order model indicate that this model is not obeyed by the system (Table 5). On the other hand, values of $q_{e(\text{theo})}$ are found to be very close to $q_{e(\text{exp})}$ for pseudo-second-order model. The percent deviation (P) values are well within the range for the sorption of Cu(II) and Cd(II) on NOC. The values of correlation coefficients (r^2) are very high for pseudo-second-order model as compared to pseudo-first-order rate model. It is therefore confirmed that sorption of Cu(II) and Cd(II) on NOC follows pseudo-second-order rate equation.

The present studies showed that Neem oil cake is a biodegradable low cost biosorbent available abundantly in India. It is used as a bio-pesticide for organic farming. The advantage of using oil cake as a sorbent is that its decomposition is faster than other bulky organic biomass due to low C/N ratio. Increase in sorption dose increases removal efficiency of Cu(II) and Cd(II). Removal efficiency also increases by increasing temperature.

The magnitude of the mean free energy indicates that sorption of Cu(II) and Cd(II) occurs via chemisorption. The values of %deviation (P) and regression coefficient (r^2) suggest that both Langmuir and Freundlich models are well obeyed. The kinetics models for the sorption of Cu(II) and Cd(II) on NOC confirms better applicability of pseudo-second-order rate equation as evident from percent deviation (P) and regression coefficient values.

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