

Equilibrium, kinetic and thermodynamic modeling for the adsorption of heavy metals onto chemically modified hydrotalcite

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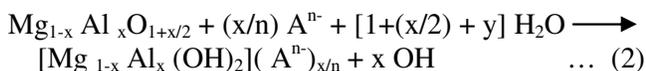
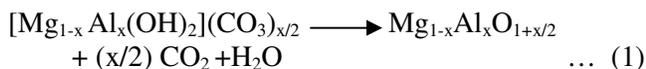
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The adsorption of heavy metals (Cu(II), Zn(II) and Cd(II)) from aqueous solutions with tannin-immobilized calcined hydrotalcite (TA-HTC) was studied using batch experiment technique. The surface characterizations of the adsorbent were investigated. Kinetic modeling of removal of metals was done using a pseudo-second-order rate expression. The intraparticle mass transfer diffusion of metals on adsorbent represented the rate-limiting step, with the activation energy of 27.05, 24.22 and 21.96 kJ/mol for Cu(II), Zn(II) and Cd(II), respectively. Experimental results showed that the adsorption of metals was selective to be in the order of Cu(II)>Zn(II)>Cd(II). Equilibrium isotherm data for metal ions were analyzed by the Langmuir, Freundlich, Dubinin-Radushkevich and Scatchard equations. The Langmuir adsorption isotherm described the adsorption data very well at all studied temperatures. Thermodynamic parameters such as standard enthalpy (ΔH°), standard entropy (ΔS°), standard free energy (ΔG°), activation energy and isosteric enthalpy and entropy were calculated and the results are discussed in detail.

Keywords: Hydrotalcite, Heavy metals, Adsorption, Isotherms, Kinetics, Thermodynamics

Hydrotalcites (HTs) are layered double hydroxides, also known as anionic clays, with a general formula, $[M_{1-x}^{2+} M_x^{3+}(\text{OH})_2]^{x+} [A_{x/n}^{n-} m\text{H}_2\text{O}]^{x-}$, where M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively and A^{n-} is an n-valent anions and x can have values between 0.20 and 0.33. HTs have positively charged brucite layers constructed from edge-sharing $\text{Mg}(\text{OH})_6$ and $\text{Al}(\text{OH})_6$ octahedra which are neutralized with interlamellar anions and water molecules. These anions and water molecules can be exchanged with other anions and polar molecules hence HTs are generally used as anion exchanger. The calcined product, HTC ($\text{Mg}_{1-x}\text{Al}_x\text{O}_{1+x/2}$) has a memory effect and therefore it is possible to reconstruct the original HT from aqueous solutions containing anions as expressed by Eqs (1) and (2):

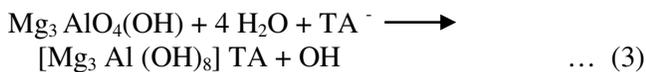


The ability to remove anions is what makes the 'memory effect' of hydrotalcites so useful. They can be used effectively as adsorbents to remove harmful

anions, both organic and inorganic¹⁻⁵ from aqueous solutions. Moreover the ability of HTC to recover its structure provides the potential for reuse and recycle of the adsorbent, which is very important in wastewater treatment.

In general, the properties of clay minerals used as adsorbents can be improved through surface modification. Modified clays can have hydrophobic surfaces, extended interlayer distance, and optimized rheological behaviour, and for these purposes, the use of surface modified HTC with chelating agents such as ethylenediamine tetraacetate (EDTA) and nitrilotriacetate (NTA) to form HTC/surfactant complexes^{6,7} for the removal of cations from aqueous systems is very common. To adsorb cations, the modified surface must either possess negatively charged exchange sites, or there should be replacement of weakly held counter ions of the modifier by more strongly held adsorbate counter ions. One of such work on use of calcined and uncalcined HTs as adsorbent has demonstrated high adsorption potential for tannin (TA) from aqueous solutions and coir industry effluents⁸. This study showed that when TA molecule comes near reaction sites on the clay surface, ion exchange between TA

and carbonate ions in the adsorbents as well as participation in the reconstruction of the HTC according to the reaction is favoured.



Moreover TA adsorption on HTC was not completely reversible and the bonding between the HTC and adsorbed TA is likely to be strong. In the present work it was decided to investigate the possibility of TA adsorbed HTC as adsorbent for the subsequent adsorption of heavy metals from aqueous solutions using its chemically reactive functional groups, including phenolic hydroxyls, carboxyls, and aromatic units which give tannin the ability to interact with metal ions through adsorption, ion-exchange, and complexation mechanisms. Till date no attempt has been made to examine the applicability of the spent HTs as adsorbents for heavy metal ions from aqueous solutions. The aim of the present study was therefore to carry out a thorough investigation of the adsorption of heavy metal ions (Cu(II), Zn(II) and Cd(II)) onto TA-immobilized HTC (TA-HTC).

Experimental Procedure

Materials

The heavy metal salts used in this study ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ and ZnCl_2) and tannin (all of reagent grade) were purchased from Fluka, Switzerland and were used as received. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Na_2CO_3 , NaOH and HCl were obtained from E. Merk, India Ltd. All solutions were prepared with deionised water of specific conductivity less than $1 \mu\text{ohm/cm}$.

Adsorbent (TA-HTC) preparation

In order to prepare the calcined hydrotalcites (HTC), the co-precipitation method proposed by Pavlovic *et al.*⁹ was used. An aqueous solution (250 mL) containing 0.75 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added drop wise under vigorous mechanical stirring into 500 mL solution containing 1.7 mol of NaOH and 0.5 mol of Na_2CO_3 . The resulting slurry was heated to 70°C for 24 h followed by filtration and washing with deionised water and was then dried at 120°C . The product (HT) was ground and sieved for particle size of 80–230 mesh. This was then calcined in a muffle furnace at 500°C for 2 h. The final product HTC was cooled to 30°C and placed in a desiccator.

TA (3.98 mmol) was loaded to 10 g HTC at pH 4.0 by the equilibrium adsorption of TA from aqueous solution followed by drying in air at 70°C . The adsorbent (TA-HTC) was filtered and washed with water and then dried at 70°C in air. The adsorbent with an average particle size of 0.096 mm was used for adsorption experiments.

Measurements

The surface area of the HT, HTC and TA-HTC was analyzed using a Quantasorb (QS-7) surface area analyzer that uses a nitrogen adsorption-desorption method. The total pore volume was determined from the amount of N_2 adsorbed at a relative pressure of 0.95. The amount of carbon in HT, HTC and TA-HTC was determined using a CHN analyzer (Carlo Erba-1361). FTIR analysis of the adsorbent samples was performed on a Shimadzu FTIR model 1801. The TGA curves of the samples were taken from a Mettler TG 50 (Shimadzu Kyoto) in air. A Systronic microprocessor pH meter (model μ -362) was used for pH measurements. A GBC Avanta (A 5450) atomic absorption spectrophotometer (AAS) with copper/cadmium/zinc hollow cathode lamps and air acetylene flame was used for determining Cu(II), Cd(II) and Zn(II) ions in solution.

Adsorption experiments

The adsorption studies were conducted by batch equilibrium method. Fifty mL of metal solution [Cu(II), Zn(II) and Cd(II)] containing 100 mg of the adsorbent (TA-HTC) in a 100 mL Erlenmeyer flask was agitated at 200 rpm in a temperature controlled water bath shaker. The effect of solution pH was studied in the pH range 2.0–8.0 with an initial concentration of 25 and 50 mg/L. Initial pH values were adjusted using 0.1 M NaOH or 0.1 M HCl solution. Ten different concentrations of metal ions between 10 and 400 mg/L were used for isotherm studies. For kinetic experiments 100 mg/L metal concentration was used. The pH of the solution was maintained at a definite value, 6.0. The adsorbed amount of metal ions was calculated from the difference between the initial and final concentrations as determined by AAS.

Results and Discussion

Adsorbent (TA-HTC) characterization

The BET surface area and the total pore volume of TA-HTC were determined from the N_2 adsorption

data and values were found to be 48.9 m²/g and 0.47 mL/g, respectively. The carbon content of the TA-HTC was found to be 36.2%. After tannin loading, the pH_{pzc} of HTC decreased from 8.4 to 6.0, indicating that the TA-HTC became more negative and at pH above 6.0 the surface charge of the TA-HTC has a negative charge, but below that pH it has a positive charge.

FTIR spectral studies

The FTIR spectra of HTC, TA-HTC and Cu(II) adsorbed TA-HTC are shown in Fig. 1. The broad band observed in the HTC spectrum around 3490 cm⁻¹ is due to the vibration of structural OH⁻ groups from the brucite-like layers. The peak at about 1640 cm⁻¹ is assigned to HOH deformation ($\delta_{\text{H-O-H}}$) confirming the presence of water molecules in the interlayer region of the HTC. The FTIR spectrum of the TA-HTC shows band characteristics of the aliphatic CH stretching at 2920 cm⁻¹ and broad band in the region 3500 cm⁻¹ due to phenolic OH stretching. Another feature in TA-HTC spectrum is the bands at 1394 and 1620 cm⁻¹ attributed to the symmetrical and asymmetrical vibrations of COO⁻, the band at 1617 cm⁻¹ corresponding to the stretching C=C groups in aromatic rings. In the spectrum of the Cu(II)-TA-HTC the peak at 1368 cm⁻¹ is indicative of the C-O stretching at the benzene ring when Cu(II) gets coordinated with oxygen. The band at 517 cm⁻¹ represents Cu-O band.

Thermal analysis of adsorbent

Thermal stability is one primary property of an adsorbent material. To determine the mass loss steps, degradation process and the thermal stability of adsorbent, TG and DTG analysis were conducted. The TG and DTG curves for HTC and TA-HTC are shown in Fig. 2. In HTC there is three-stage decomposition which can be listed as follows.

1. Removal of adsorbed water (90-200°C) with a weight loss of 9.0% which include physioadsorbed (upto 100°C) and interlayer water (110-200°C).
2. Dehydroxylation (300-380°C) with a weight loss of 19.0% which include partial loss of OH groups in the brucite-like layer (323°C) and loss of OH groups bonded to intercalated anion (up to 380°C).
3. Decarbonation (380-680°C) with a weight loss of 36.0% which include solvated CO₃²⁻ and that

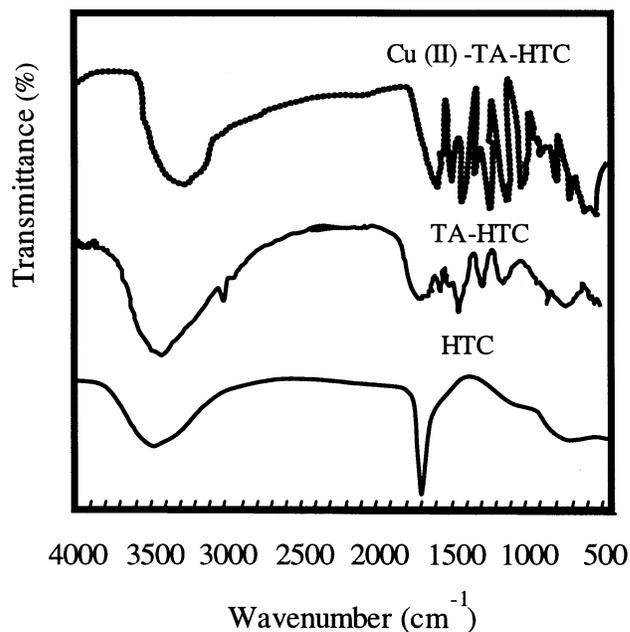


Fig. 1—FTIR spectra of HTC, TA-HTC and Cu-TA-HTC.

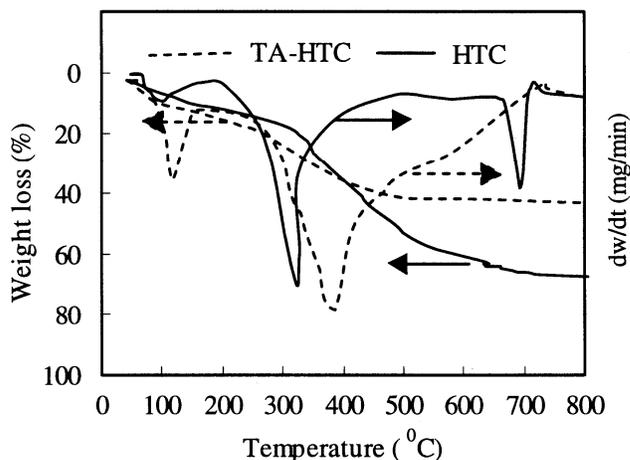


Fig. 2—TG/DTG curves of HTC and TA-HTC.

bonded to OH layer. The carbonate anions in the hydrotalcite structure decompose to carbon dioxide (CO₂) and O²⁻, leaving the O²⁻ anions retained between the layers¹⁰.

But in the case of TA-HTC, there are only two stages of decomposition, first occurs at 103°C with a weight loss of 10.3% due to dehydration. The second decomposition of TA-HTC occurs at 392°C, in which a weight loss of 30.0% is produced by dehydroxylation and also by the decomposition of tannin. So one can assume that the thermal stability of HTC increased with tannin loading.

The thermogravimetric analysis has proved to be a useful analytical technique in evaluating kinetic parameters of thermal degradation reaction such as energy of activation (E_a), enthalpy of activation (ΔH), entropy of activation (ΔS), free energy of activation (ΔG), order of reaction (n) and frequency factor (Z), which provides valuable quantitative information regarding the stability of the adsorbents. Various methods have been proposed by different investigators to estimate the kinetic parameters of thermal degradation reaction. Of all the various differential methods known, one that is widely used is the Freeman-Carroll method¹¹.

$$\frac{-E_a}{2.303R} \Delta \left(\frac{1}{T} \right) = -n + \frac{\Delta \log \left(\frac{dW}{dT} \right)}{\Delta \log (W_\infty - W)} \quad \dots (4)$$

where W_∞ is the maximum mass loss; W the total mass loss upto time T and E_a is the activation energy. The values of $(W_\infty - W)$ and dW/dT were determined from TG and DTG curves, respectively, in terms of 20 divisions. The plots of $\Delta \log \left(\frac{dW}{dT} \right)$ against $\Delta \left(\frac{1}{T} \right)$ were a straight line and the slope and intercept of which gave the values of E_a and n , respectively (Figure not shown). The values of E_a , which measure the minimum energy required for sample decomposition were found to be 15.12 and 16.84 kJ/mol and the values of n were found to be 1.46 and 1.24 for HTC and TA-HTC, respectively. Lower activation energy during decomposition of HTC is an evidence of early thermal decomposition of HTC when compared to TA-HTC and is a clear evidence of high thermal stability of TA-HTC.

To calculate the enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger), free energy of activation (ΔG^\ddagger) for thermal degradation reaction of HTC and TA-HTC, the following equations were employed, respectively¹²:

$$\Delta S^\ddagger = 2.303R \log (Zh / kT) \quad \dots (5)$$

where frequency factor Z is given by $Z = 10^{\text{intercept}}$ and h and k are Plank's and Boltzmann's constants, respectively.

$$\Delta H^\ddagger = E_a - RT \quad \dots (6)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad \dots (7)$$

The values of Z , ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger were found to be 29.08 s⁻¹, 9.13 kJ/mol, -224.25 J/mol and 170.41 kJ/mol, respectively for HTC and 17.7 s⁻¹, 10.05 kJ/mol, -228.31 J/mol and 174.21 kJ/mol, respectively for TA-HTC. Due to abnormally low value of frequency factor [Z] the thermal degradation of HTC and TA-HTC were thought to be a slow reaction which is further supported by the low and negative value of entropy [ΔS^\ddagger]. However, the negative values of ΔS^\ddagger indicate the formation of highly ordered activated complex, and the degrees of freedom of rotation and vibration are less than the values anticipated in the non activated complex¹³. The positive values of ΔG^\ddagger indicate that the thermal degradation of HTC and TA-HTC was non spontaneous.

Effect of pH

The pH of the solution is most significant factor in adsorption of heavy metals as it has a major effect on the protonation and deprotonation of the adsorbent and adsorbate functional groups. Figure 3 shows the effect of pH on Cu(II), Cd(II) and Zn(II) adsorption. As evident from the Fig., Cu(II), Cd(II) and Zn(II) ions were best adsorbed onto TA-HTC at pH range 5.5-7.0. A maximum adsorption of 99.7 and 95.0% for Cu(II), 98.9 and 93.1% for Zn(II) and 97.2 and 91.3% for Cd(II) was observed at an initial concentration of 25 and 50 mg/L at pH 6.0. According to the simple speciation diagrams which were constructed by earlier workers¹⁴⁻¹⁶ for Cu(II), Cd(II) and Zn(II), respectively, all the species occurring at pH values of 7.0 and below carry a positive charge either as Cu²⁺, Cu(OH)⁺, Cd²⁺, Cd(OH)⁺, Zn²⁺ or Zn(OH)⁺. Moreover it has been shown that the final pH is always less than the initial pH. When the initial pH of the reaction mixture varied between 3.0 and 6.0, the final pH of the reaction medium remained between 2.6 and 4.4 for Cu(II), 2.6 and 4.7 for Cd(II) and 2.8 and 5.2 for Zn(II) at an initial concentration of 25 mg/L, similar variations were observed for 50 mg/L also. This shift in solution pH towards acidic region further confirmed the cation exchange mechanism being in operation in metal cations adsorption by releasing protons from the weakly acidic carboxyl groups and phenolic OH groups of TA present in TA-HTC. Because the pKa value of carboxyl group is in the range of 4.0-6.0, more carboxyl groups will be deprotonated at pH over this range, and thus resulting in more negative binding sites so that adsorption process is more effective. In

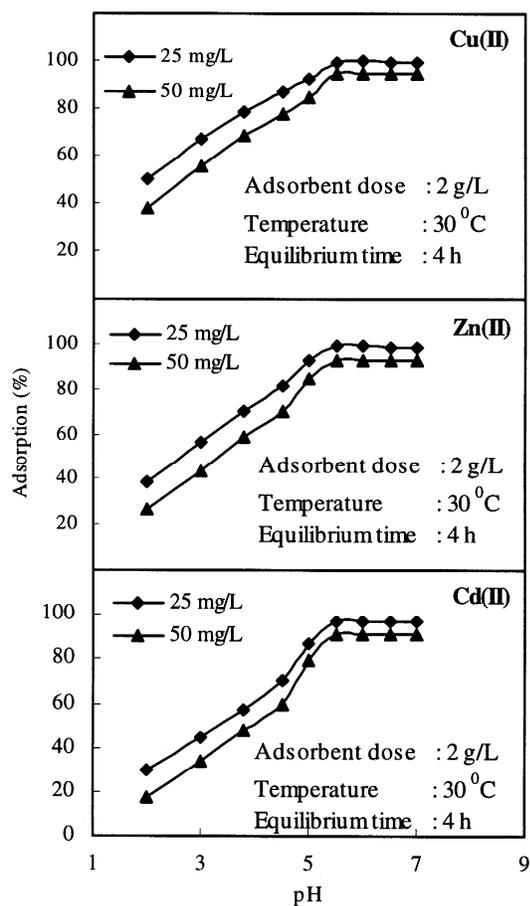


Fig. 3—Effect of pH on the adsorption of Cu(II), Zn(II) and Cd(II) onto TA-HTC.

the experiments performed at pH between 2.0 and 5.5, the increase in positively charged surface sites as pH decreases led to the increase of the electrostatic repulsion between the surface positive charges and the positively charged metal ions and therefore caused the decrease of the adsorption capacity of the adsorbent. In addition, H^+ ions may compete with metal cations (M^{2+}), for adsorption sites; at lower pH, the concentration of H^+ ions is higher, thus leading to a lower adsorption of metal ions. As the pH increased the degree of protonation of the surface functional groups gradually reduced and approached zero at pH 6.0 (pH_{pzc}) resulting in a gradual increase in the adsorption. Above pH 6.0, the surface of the adsorbent is negative and the metals, Cu(II), Cd(II) and Zn(II) are still present as $M(OH)^+$ ions and under this conditions these metals are adsorbed through a favourable electrostatic attraction. Hence, the optimum pH was selected as 6.0 for adsorption of Cu(II), Cd(II) and Zn(II) ions onto TA-HTC.

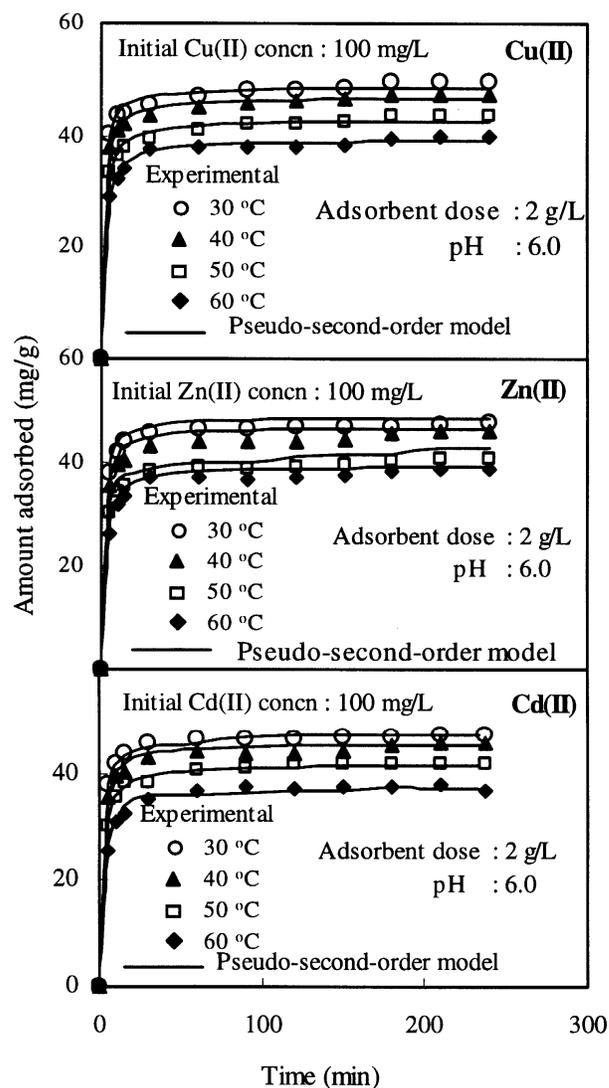


Fig. 4—Effect of contact time and temperature on the adsorption of Cu(II), Zn(II) and Cd(II) onto TA-HTC.

Adsorption kinetics

The influence of contact time on the adsorption of Cu(II), Cd(II) and Zn(II) ions (100 mg/L) onto TA-HTC (Fig. 4) was investigated at various temperatures, i.e., 30, 40, 50 and 60°C. It has been observed that the metal adsorption rate is high at the beginning upto 10 min and thereafter rose slowly till a saturation level was reached at 180 min. The initial rapid phase may be due to greater number of adsorption sites available for the adsorption of metal ions. The ion exchange process is the major mechanism for the removal of metal ions. With increase in temperature from 30 to 60°C, the amount of metal adsorbed increased from 40.05 to 49.87 mg/g for Cu(II), 38.51 to 47.52 mg/g for Zn(II) and 38.00

to 45.80 mg/g for Cd(II), while the percentage removal increased from 80.1 to 99.7% for Cu(II), 77.0 to 95.1% for Zn(II) and 76.0 to 91.6% for Cd(II), thereby indicating that the metal removal by adsorption on TA-HTC is endothermic. Similar endothermic nature of the adsorption process has been reported for other adsorbent systems¹⁷⁻¹⁹. The enhanced adsorption with temperature may be attributed to either increase in the number of active binding sites available for adsorption on the adsorbent surface or due to the decrease in the boundary layer thickness surrounding the adsorbent, and thereby decreased boundary layer mass transfer resistance owing to the decrease in the viscosity of the solution.

Kinetic models

Due to the fast decrease in concentration of metal ions in solution at a short time of contact, implying the strong electrostatic interaction between the negatively charged TA-HTC surface and metal cations, the pseudo-second-order rate expression given by Ho²⁰ is used to fit the kinetics of metal ion exchange on TA-HTC.

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad \dots (8)$$

In the above equation, q_e and q_t are the amounts of metal ions adsorbed at equilibrium and at a time t , respectively and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second-order rate constant. The kinetic parameters were calculated by non-linear regression analysis. The

calculated values of k_2 and q_e and their corresponding regression coefficients (R^2) and chi-square (χ^2) values are presented in Table 1. The results suggest that metal ions adsorption by TA-HTC can be best described by pseudo-second-order rate expressions. It may also be found from Table 1 that the calculated q_e values are very close to that of experimental q_e values, thus it may further be confirmed that the adsorption of metal ions onto TA-HTC can be best explained by pseudo-second-order. The values of k_2 and q_e increased with increase of temperature; therefore, this process is controlled by diffusion kinetics.

The apparent activation energy gives an idea about the influence of temperature on diffusivity. The activation energy, E_a , was obtained from the Arrhenius equation, which is given as follows:

$$\ln k_{ad} = \ln A - \frac{E_a}{RT} \quad \dots (9)$$

where E_a is the activation energy (kJ/mol), k_{ads} is the sorption rate constant, A is the Arrhenius constant, R is the gas constant (8.314 J/mol/K), and T is the solution temperature (K). k_{ads} is the pseudo-second-order rate constant. The plots of $\ln k_{ad}$ versus $1/T$ were found to be straight lines and the values of E_a were determined from the slope of linear plots. The values were found to be 27.05, 24.22 and 21.96 kJ/mol for Cu(II), Zn(II) and Cd(II) ions, respectively. The positive values of E_a suggest that increase in temperature favours the adsorption. Consequently, the adsorption process is endothermic in nature. Some of the assigned values of E_a (kJ/mol) include 8.0–25.0 to

Table 1—Kinetic parameters for the adsorption of Cu(II), Zn(II) and Cd(II) onto TA-HTC.

Metal ion	Temperature (°C)	k_2 (mg/g/min)	q_e , cal (mg/g)	q_e , exp (mg/g)	R^2	χ^2
Cu(II)	30	1.35×10^{-2}	39.09	40.05	0.997	0.32
	40	1.45×10^{-2}	42.92	43.53	0.995	0.66
	50	2.60×10^{-2}	46.84	47.53	0.996	0.75
	60	3.28×10^{-2}	48.72	49.87	0.995	0.94
Zn(II)	30	1.31×10^{-2}	37.02	38.51	0.995	0.51
	40	1.41×10^{-2}	40.42	41.67	0.997	0.34
	50	2.43×10^{-2}	45.53	46.41	0.998	0.41
	60	2.86×10^{-2}	46.74	47.52	0.996	0.52
Cd(II)	30	0.97×10^{-2}	35.11	38.00	0.996	0.44
	40	1.42×10^{-2}	38.53	40.86	0.991	0.86
	50	2.14×10^{-2}	44.19	42.54	0.995	0.67
	60	1.83×10^{-2}	41.90	45.80	0.995	0.78

physical adsorption, less than 21.0 to aqueous diffusion and 20.0–40.0 to pore diffusion²¹. In this study, the calculated values of E_a are in the range of pore diffusion, suggesting that metal adsorption onto TA-HTC is of pore diffusion-controlled adsorption as the rate-limiting processes.

Mass transfer aspects of metal adsorption onto TA-HTC

Both external mass transfer model and intraparticle mass transfer diffusion model [Eqs (10) and (11), respectively] are used for the dynamic analysis of metal adsorption onto TA-HTC.

$$\left[\frac{d(C/C_0)}{dt} \right]_{t \rightarrow 0} = -B_L S \quad \dots (10)$$

$$f(q_t/q_e) = -\left[\log \left(1 - (q_t/q_e)^2 \right) \right] = 4\pi^2 D_i t / 2.3d^2 \quad \dots (11)$$

where B_L is the external mass transfer coefficient (cm/s) and S is the specific surface area for mass transfer. C and C_0 is the concentration of solute in the solution and the initial concentration (mg/L), respectively. D_i is the diffusion coefficient in the solid (cm²/s) and d the particle diameter. The values of B_L and D_i for different temperatures were determined from the plots of C/C_0 versus t and $\log[1 - (q_t/q_e)^2]$ versus t , respectively (Figures not shown) and the results are presented in Table 2. As shown in Table 2, the B_L values increased from 1.74×10^{-4} to 2.16×10^{-4} , 1.56×10^{-4} to 2.08×10^{-4} and 1.00×10^{-4} to 1.95×10^{-4} cm/s, for Cu(II), Zn(II) and Cd(II) ions, respectively when temperature increased from 30 to 60°C. The B_L values suggest that the velocity of metal transport from the bulk solution to the solid phase is quite rapid, and this substantiate the favourable physical and chemical characteristics anticipated for TA-HTC for use as an adsorbent for the treatment of metal bearing wastewaters²². The D_i values are also increased from 1.64×10^{-13} to 2.31×10^{-13} , 1.49×10^{-13} to 1.89×10^{-13} and 1.32×10^{-13} to 1.71×10^{-13} cm²/s, for Cu(II), Zn(II) and Cd(II) ions, respectively when temperature increased from 30 to 60°C. The increase in mass transfer coefficients with increasing temperature is due to enhanced diffusion of metal ions in the boundary layer and a decrease in retarding forces acting on the diffusing ions as a consequence of a higher thermal agitation when temperature is increased from 30 to 60°C. According to the earlier reports²³ the values of D_i in the range 10^{-11} – 10^{-13} cm²/s

reflects pore diffusion as the rate-limiting step. It appeared that the rate-limiting step to be pore diffusion process since the magnitudes of the coefficient for all metals are in the order of 10^{-13} cm²/s. This is consistent with the available data in the literature reporting the D_i values to be 6.68×10^{-13} , 2.77×10^{-13} and 2.35×10^{-12} cm²/s for the adsorption of Cu(II) onto activated slug, KRF-10p cation exchanger and kraft lignin, respectively^{24–26}, 0.18×10^{-11} cm²/s for the adsorption of Zn(II) onto Zeolite A²⁶ and 2.30×10^{-12} , 0.33×10^{-11} and 8.0×10^{-11} cm²/s for the adsorption of Cd(II) ions onto kraft lignin, Zeolite A and chitosan-coated beads, respectively^{26–28}.

Kinetic data were further tested using Bangham's equation²⁹ in order to confirm whether pore diffusion is the only the rate-limiting step.

$$\log \log \left(\frac{C_0}{C_0 - q_t m} \right) = \log \left(\frac{k_b m}{2.303V} \right) + \alpha \log(t) \quad \dots (12)$$

where C_0 is the initial concentration of metal ion in solution (mg/L), V is the volume of solution (50 mL), m is the weight of TA-HTC per liter of solution (2 g/L), q_t (mg/g) is the amount of metal ion retained at time t , α (<1) and k_b are constants. If the experimental data is represented by this equation then the adsorption kinetics are limited by the pore diffusion³⁰. The slope and intercept of double logarithmic plot according to above equation gives the values of α and k_b . The Bangham's constants calculated from the plots are also represented in Table 2. It can be seen that the values of α and k_b varied as a function of solution temperature. The higher correlation of experimental data with Bangham equation still confirmed that the pore diffusion is significant in the rate-controlling step.

Adsorption isotherms

The equilibrium data at different temperatures were modeled using Langmuir, Freundlich and Dubinin-Radushkevich adsorption models³¹:

$$\text{Langmuir : } q_e = Q^0 b C_e / (1 + b C_e) \quad \dots (13)$$

$$\text{Freundlich: } q_e = K_F C_e^{1/n} \quad \dots (14)$$

Dubinin- Radushkevich (DR):

$$q_e = x_m (\epsilon^2)^{-\beta} \quad \dots (15)$$

Table 2—Mass transfer parameters for the adsorption of Cu(II), Zn(II) and Cd(II) onto TA-HTC.

Metal ion	Temperature (°C)	D_i (cm ² /s)	R^2	B_L (cm/s)	R^2	α	K_b	R^2
Cu(II)	30	1.64×10^{-13}	0.983	1.74×10^{-4}	0.665	0.138	35.73	0.974
	40	2.04×10^{-13}	0.986	1.81×10^{-4}	0.546	0.150	38.58	0.949
	50	2.15×10^{-13}	0.976	2.06×10^{-4}	0.467	0.186	41.53	0.992
	60	2.31×10^{-13}	0.991	2.16×10^{-4}	0.678	0.260	42.88	0.986
Zn(II)	30	1.49×10^{-13}	0.995	1.56×10^{-4}	0.554	0.113	34.51	0.939
	40	1.63×10^{-13}	0.986	1.67×10^{-4}	0.465	0.143	37.03	0.978
	50	1.70×10^{-13}	0.978	2.01×10^{-4}	0.634	0.157	41.15	0.984
	60	1.89×10^{-13}	0.965	2.08×10^{-4}	0.586	0.171	42.49	0.952
Cd(II)	30	1.32×10^{-13}	0.967	1.00×10^{-4}	0.698	0.109	32.57	0.912
	40	1.42×10^{-13}	0.956	1.55×10^{-4}	0.465	0.121	33.54	0.959
	50	1.69×10^{-13}	0.967	1.86×10^{-4}	0.543	0.147	37.48	0.909
	60	1.71×10^{-13}	0.978	1.95×10^{-4}	0.335	0.158	39.46	0.983

The Langmuir model assumes monolayer adsorption on a surface with a finite number of identical sites, that all sites are energetically equivalent and that there is no interaction between adsorbed solutes. The Langmuir constants Q^0 (mg/g) and b represents the amount of solute adsorbed per unit weight of adsorbent required for monolayer coverage of the surface and the heat of adsorption, respectively. The Freundlich equation is an empirical expression based on adsorption onto a heterogeneous surface. K_F and $1/n$ are the Freundlich constants, indicating adsorption capacity and adsorption intensity, respectively. This isotherm usually fits the experimental data over a wide range of concentrations. The D–R isotherm model explains the physical and chemical characterization of adsorptions. In D-R equation x_m (mg/g) is the maximum adsorption capacity, β is the activity coefficient related to mean sorption energy, and ε is the Polanyi potential, which is equal to

$$\varepsilon = RT \ln(1 + 1/C_e) \quad \dots (16)$$

where R is the gas constant (kJ/mol/K) and T is the temperature (K). The adsorption potential is independent of the temperature that varies according to the nature of adsorbent and adsorbate.

The adsorption constants of Cu(II), Zn(II) and Cd(II) ions onto TA-HTC were calculated according to the Langmuir, Freundlich and DR sorption models using non-linear regression analysis and the results are listed in Table 3. Based on correlation coefficient

(r^2) values (> 0.99) and chi-square (χ^2) values ($< 2.0\%$) for all metals, it was found that in all the temperature ranges (30 to 60°C) the adsorption isotherm data of TA-HTC can be best described by the Langmuir model. Results obtained from the Langmuir model indicated that q_e values obtained from the Langmuir model are close to the experimental q_e values (Fig. 5). The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on TA-HTC, while the percentage adsorption versus pH plots shown earlier clearly suggested two or more sites with different affinities towards metal ions. It has already been demonstrated that the Langmuir isotherm equation gives adequate results for metal adsorption onto various adsorbents where surface heterogeneity is known to be present³². According to Q^0 parameter, adsorption onto TA-HTC is produced in the following sequence Cu(II)>Zn(II)>Cd(II). This affinity order is in agreement with the rule for the sequence of complex stability from the Irving-Williams concept based on ligand field or simple-crystal field theory³³. According to this rule, the stability of complexes of metal cations-oxygen donor groups decreases in the series: Cu(II)>Zn(II)>Cd(II). A similar trend in variation was reported by other researchers also³⁴. This general trend may also explained by the fact that metal ions with smaller ionic radius diffuse faster in aqueous systems. Therefore, the metal ion with a smaller ionic radius ($\text{Cu}^{2+} = 0.73 \text{ \AA}$) would easily react with adsorbent resulting in a greater surface coverage than those with

larger ionic surface ($Zn^{2+}=0.74 \text{ \AA}$; $Cd^{2+}= 0.97 \text{ \AA}$). The adsorption energy (E_{D-R}) was calculated using the following relationship of DR equation:

$$E_{D-R} = 1/\sqrt{-2\beta} \quad \dots (17)$$

The value of E_{D-R} gives information about the type of adsorption mechanism as chemical ion-exchange or physical adsorption. A value of E_{D-R} between 8.0 and 16.0 kJ/mol corresponds to ion-exchange process whereas values <8.0 kJ/mol represent a physical type of process. In the present study for three metal ions the values of E_{D-R} (Table 3) were calculated to be between the values of 8.0 and 16.0 kJ/mol. It may be suggested that ion exchange is the major mechanism responsible for the metal adsorption process³⁵.

Scatchard plot analysis

In order to achieve more comprehensive information about the affinity of binding sites and to analyze the results of adsorption isotherms, the Scatchard plot analysis, also called independent site-oriented model³⁶ was applied to the experimental data. Compared to other mathematical transformations of the classical Langmuir equation, awareness about the equilibrium concentration ranges where the Langmuir model shows good fit to the experimental data can be acquired more easily through the Scatchard equation which is represented as follows:

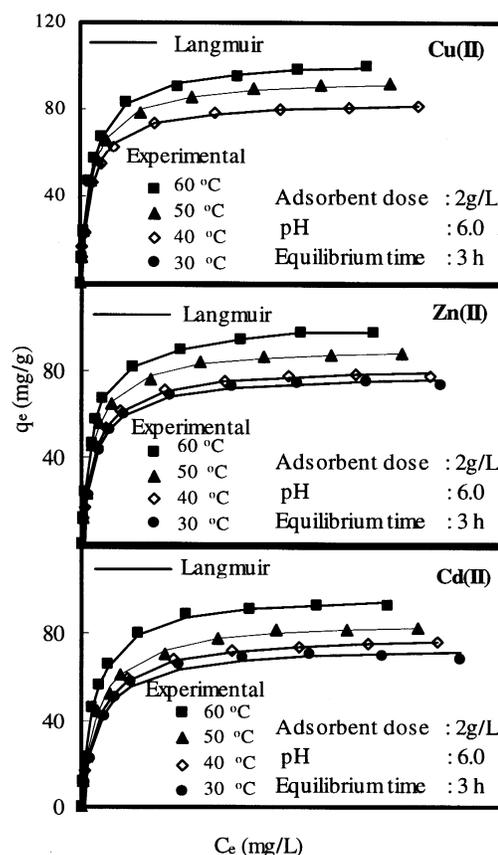


Fig. 5—Comparison of the experimental (dots) and Langmuir isotherm model (line) fits for the adsorption of Cu(II), Zn(II) and Cd(II) onto TA-HTC.

Table 3—Isotherm parameters for the adsorption of metal ions onto TA-HTC.

Langmuir Temp. (°C)	Langmuir Q^0 (mg/g)	Freundlich		Dubinin-Radushkevich									
		b (L/mg)	r^2	χ^2	K_F	1/n	r^2	χ^2	χ_m (mg/g)	β (mol ² kJ ⁻²)	E_{D-R} (kJ/mol)	r^2	χ^2
Cu(II)													
30	81.4	0.115	0.997	1.2	24.9	0.226	0.936	8.6	29.8	0.0061	9.1	0.931	9.4
40	84.8	0.131	0.995	3.5	26.6	0.223	0.932	6.7	31.6	0.0031	12.0	0.944	8.5
50	94.7	0.127	0.999	4.3	28.1	0.238	0.938	7.6	33.7	0.0027	13.4	0.938	9.1
60	103.5	0.121	0.997	4.6	29.4	0.249	0.935	9.5	35.5	0.0021	15.2	0.955	12.3
Zn(II)													
30	78.9	0.099	0.999	1.1	23.0	0.233	0.923	6.6	27.7	0.0064	8.8	0.921	8.2
40	81.9	0.108	0.997	1.7	24.2	0.232	0.926	8.4	29.1	0.0043	10.7	0.932	8.1
50	91.5	0.117	0.996	3.3	26.5	0.240	0.927	7.6	32.1	0.0039	11.2	0.978	7.6
60	101.7	0.123	0.998	1.3	28.6	0.250	0.928	9.3	34.8	0.0033	12.1	0.983	8.5
Cd(II)													
30	74.9	0.082	0.997	1.1	20.7	0.238	0.914	5.3	25.2	0.0070	8.4	0.901	8.6
40	80.1	0.084	0.995	2.5	21.2	0.248	0.935	5.9	26.0	0.0052	9.7	0.989	6.6
50	86.7	0.089	0.993	4.4	22.8	0.254	0.947	9.8	27.9	0.0048	10.1	0.909	6.9
60	98.7	0.104	0.996	3.3	26.8	0.252	0.918	7.6	32.8	0.0041	11.0	0.968	13.1

$$\frac{q_e}{C_e} = Q^0 b - q_e b \quad \dots (18)$$

where q_e and C_e are the equilibrium metal adsorption capacity of the adsorbent and the equilibrium metal concentration in the aqueous solution, respectively, and Q^0 and b are the adsorption isotherm parameters. The shape of the scatchard plot is related to the type of the interactions of adsorbate with the adsorbent. If a straight line is obtained by plotting q_e/C_e versus q_e , then the adsorbent presents only one type of binding sites and if scatchard plot shows a deviation from linearity, the adsorbent presents more than one type of binding sites³⁷. Taking the sorption of metal ions on various adsorbents, the studies dealing with the applicability of Scatchard plot analysis are very few. However, it is well known that TA-HTC can interact with metal ions through multiple mechanisms, such as dispersive forces, diffusion, ion exchange and complex formation. The observed deviations from the linearity in the Scatchard plot of metal adsorption by TA-HTC (Fig. 6) is attributed to the different affinities of the binding sites towards metal ions, i.e., high-affinity (H) and low-affinity (L) binding sites. It can be thought that the carboxyl groups of TA exhibiting relatively low pK_a values and those have suitable conformations for metal binding are thought to construct the main high-affinity (strong) binding

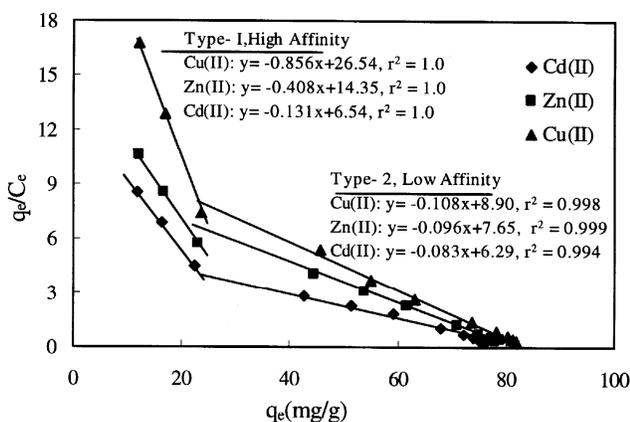


Fig. 6—Scatchard plots for the adsorption of Cu(II), Zn(II) and Cd(II) ions onto TA-HTC.

sites, while the phenolic hydroxyls exhibiting relatively high pK_a values are believed to be the main low-affinity (weak) binding sites. The binding constants (b) and theoretical maximum capacities (Q^0) of high- and low-affinity binding sites were separately calculated and given in Table 4. As can be seen in Table, the values of b and Q^0 calculated from the Langmuir isotherm are very close to those calculated for low-affinity binding sites. On the basis of these results, the sorption of metal ions onto TA-HTC was mainly attributed to the low affinity binding sites, and the bindings involving the complex formations were thought to be occurred through complex formation³⁸. So, the low affinity binding is attributed to the complex formation, while the high-affinity binding is attributed to the ion-exchange mechanism in the metal ion adsorption on TA-HTC.

Adsorption thermodynamics

Thermodynamic parameters can evaluate the orientation and feasibility of the physicochemical adsorptive reaction and can provide strong information regarding the inherent energy and structural changes due to metal ion adsorption and also about the mechanism involved in adsorption process. The thermodynamic parameters of the adsorption process were determined from the experimental data obtained using the following Eqs:

$$\ln K_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \dots (19)$$

$$\Delta G^0 = -RT \ln K_d \quad \dots (20)$$

where K_d is the distribution coefficient for the adsorption ΔS^0 , ΔH^0 and ΔG^0 are the change of entropy, enthalpy and the Gibbs energy, T is the absolute temperature and R the gas constant. The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the Vant Hoff linear plots of $\ln K_a$ versus $1/T$ (Figure not shown). The results are presented in Table 5. The positive values of ΔH^0 suggest the possibility of a strong binding between metals and the adsorbent and confirm endothermic

Table 4—Scatchard parameters for metal adsorption onto TA-HTC.

	Q^0 (mg/g)			b (L/mg)		
	Cu(II)	Zn(II)	Cd(II)	Cu(II)	Zn(II)	Cd(II)
High affinity	31.01	35.12	50.05	0.856	0.408	0.131
Low affinity	82.03	79.30	75.19	0.108	0.096	0.083

Table 5—Thermodynamic parameters for Cu(II), Zn(II) and Cd(II) adsorption onto TA- HTC.

Metal ion	Temperature (K)	ΔH° (kJ/mol)	ΔS° (J/mol)	ΔG° (kJ/mol)
Cu(II)	303	19.02	74.58	-3.52
	313			-4.37
	323			-5.12
	343			-5.74
Zn(II)	303	20.21	76.64	-3.04
	313			-3.63
	323			-4.69
	343			-5.24
Cd(II)	303	22.56	81.74	-2.43
	313			-2.71
	323			-3.75
	343			-4.84

process. Entropy has been defined as the degree of disorder of the system. The positive values of ΔS° reflect good affinity of metal ions towards the TA-HTC and the increased randomness at the solid-solution interface during the adsorption of metal ions onto TA-HTC, since adsorbed metal ions led to decreasing number of water molecules surrounding metal cations and thus the degree of freedom of the water molecules increases¹⁷. Moreover it was found that $\Delta H^\circ < T \Delta S^\circ$, indicating that the influence of entropy is more remarkable than enthalpy of activation in the present work. The negative values of ΔG° show the thermodynamic feasibility and spontaneity of adsorption and also the ΔG° value decreased when the temperature increased from 30 to 60°C for all the three metal ions (Table 5), suggesting more efficient adsorption at higher temperatures. At higher temperature, ions are readily desolvated and therefore their adsorption becomes more favourable. Cu(II) shows values of ΔG° greater than that for Zn(II) and Cd(II) exhibiting a larger affinity for the reaction site than Zn(II) and Cd(II). The magnitude of ΔG° is a useful mean for evaluating the type of adsorption process. The typical range of ΔG° values for an ion exchange mechanism is 10.0-20.0 kJ/mol³⁹. The magnitude of ΔG° upto 20.0 kJ/mol is consistent with electrostatic interaction between adsorption sites and the metal ions (physical adsorption). If this magnitude lies between 21.0 and 40.0 kJ/mol, the adsorption process can be explained by complexation in which charge sharing or transfer from the adsorbent

surface to the metal ions takes place. The values of ΔG° obtained in this work range from -3.52 to -5.74 kJ/mol for Cu(II), -3.04 to 5.24 kJ/mol for Zn(II) and -2.43 to -4.84 kJ/mol for Cd(II) indicating that ion exchange may play a significant role in the adsorption process.

Isosteric heat of metal ion adsorption

The following Clausius-Clapeyron equations were used to calculate the isosteric heat (ΔH_x), the isosteric entropy (ΔS_x), of adsorption as a function of metal loading onto TA-HTC⁴⁰.

$$\frac{d(\ln C_e)}{d(1/T)} = \frac{-\Delta H_x}{R} \quad \dots (21)$$

$$\frac{d(\ln C_e)}{d(\ln T)} = \frac{\Delta S_x}{R} \quad \dots (22)$$

Using experimental adsorption isotherm data for Cu(II), Zn(II) and Cd(II) ions onto TA-HTC at different temperatures, the values of ΔH_x and ΔS_x were determined from the slope of the plots of $\ln C_e$ versus $1/T$ (Fig. 7) and $\ln C_e$ versus $\ln T$ (Figure not shown). The values of ΔH_x were increased to a small extent from 10.7 to 14.9, 16.2 to 20.9 and 17.3 to 22.8 kJ/mol for Cu(II), Zn(II) and Cd(II), respectively with increase in surface loading from 25 to 45 mg/g indicating that the surface of the TA-HTC is having energetically heterogeneous surface and there may be some lateral interactions between the adsorbed metal ions. The enthalpy is dependent on the volume of the adsorbed phase because initially the volume of the adsorbed phase is zero. The adsorptive interactions normally do not bring about any major change in surface configuration, yet considerable entropy increase from 4.1 to 5.6, 6.1 to 8.6 and 6.6 to 8.7 J/mol for Cu(II), Zn(II) and Cd(II), respectively with increase in surface loading from 25 to 45 mg/g, signifies an increased state of randomness at the solid-solution interface following adsorption. This may be attributed to the increasing disorder due to the fact that the number of the water molecules surrounding cationic metal ions decreases and thus the degree of freedom of the water molecules increases.

Comparison with other adsorbents

The adsorption capacities (Q°) for the adsorption of Cu(II) (81.47 mg/g), Zn(II) (78.91 mg/g) and Cd(II) (74.97 mg/g) onto TA-HTC were found to be higher than the ones reported in the literature. Calisir *et al.*⁴¹,

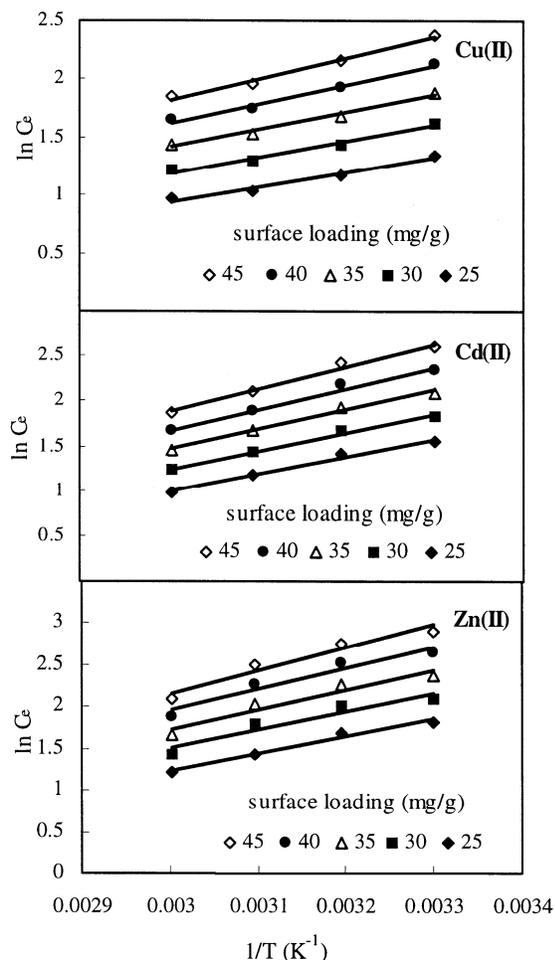


Fig. 7—Plots of $\ln C_e$ versus $1/T$ for Cu(II), Zn(II) and Cd(II) adsorption onto TA- HTC.

Ucer *et al.*⁴², Zaini *et al.*⁴³, Wang *et al.*⁴⁴, Zhou *et al.*⁴⁵, and Elya *et al.*⁴⁶, reported that the maximum adsorption capacities of recycled tire rubber, tannic acid immobilized activated carbon, cattle-manure-compost based activated carbons, organically functionalized silica gel, thiourea-modified magnetic chitosan microspheres and Na-montmorillonite/alginate microcapsules were 1.51, 2.23, 5.97, 19.9, 66.7 and 72.9 mg/g, respectively. The values of Q^0 for Zn(II) adsorption were reported to be 1.93, 8.02, 8.65, 11.4, 20.37 and 49.94 mg/g for Amizour soil⁴⁷, modified jute fiber⁴⁸, natural zeolite⁴⁹, wheat straw⁵⁰, lignimerin⁵¹ and multiwalled carbon nanotube⁵², respectively. The values of Q^0 for the adsorption of Cd(II) onto synthetic zeolite pellets⁵³, granular activated carbon treated with nitric acid⁵⁴, calcite⁵⁵, ETS-4 titanosilicate⁵⁶, thiol-functionalized silica⁵⁷ and lignite⁵⁸ were found to be 3.14, 18.48, 18.52, 26.88, 39.9 and 51.48 mg/g, respectively. In comparison, it is

clear that Q^0 values for Cu(II), Zn(II) and Cd(II) ions obtained in this study were very high.

Conclusions

Tannin immobilized calcined hydrotalcite (TA-HTC) is used as an adsorbent for the removal of heavy metals [Cu(II), Zn(II) and Cd(II)] from aqueous solutions. The maximum adsorption was found at pH 6.0. The mechanism for the removal of metal ions by TA-HTC was based on ion exchange followed by complexation. Experimental results showed that the adsorption of these metals was selective to be in the order of Cu(II)>Zn(II)>Cd(II). The process was very fast initially and maximum adsorption was observed with 3 h of agitation. The adsorption kinetics were investigated and kinetic parameters such as rate constant, external mass transfer diffusion and intraparticle mass transfer diffusion coefficients were evaluated for temperatures ranging from 30 to 60°C. Equilibrium isotherm data were analyzed by the Langmuir, Freundlich and Dubinin-Radushkevich equations using non-linear regression analysis. Scatchard plot analyses were carried out and non-linearity of Scatchard plots in the present study revealed different affinity binding sites of TA-HTC toward metal ions. Thermodynamic parameters were calculated and the Clausius-Clapeyron equation was used to calculate the isosteric enthalpy (ΔH_x) and isosteric entropy (ΔS_x) of adsorption.

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