Influence of parameters and kinetic study of nickel (II) and cadmium (III) metals on Dalbergia derived adsorbent

Priyanka Lahot[*], D.P. Tiwari

Chemical Engineering Dept., Deenbandhu Chhotu Ram University of Science and Technology Murthal Sonipat 131039 Haryana, India.

Original article

ABSTRACT

Background and aims: From the past studies, it has been proved that consumption of heavy metals by humans may cause several chronicle problems like cancer, kidney and liver damage, high blood pressure and low blood pressure problems and etc. So, it has become very crucial to remove these heavy metals from industrial wastewater. The aim of this study was to find out a low cost and easy available adsorbent for adsorption of heavy metals.

Methods: Batch removal study of nickel and cadmium metal ions from their salt solutions was used. Preparation of adsorbent was done by following chemical treatment method and finally dried product obtained was characterized through FT-IR and morphological study. Influence of parameters initial metal ion concentration, pH and adsorbent dosage were done by varying one factor remaining others fixed. Equilibrium study at different temperatures while concentration fixed and kinetic study to know efficiency of adsorbent were done.

Results: Influence of parameters gives optimum range for adsorption as pH gives 6.8 and 0.2 g for adsorbent dose. Adsorption isotherm well explained by Temkin isotherm as it gives positive value for calculating constants and high correlation coefficient 0.99. Kinetic behavior well followed by Pseudo second order, Intraparticle diffusion and Elovich second order kinetic models. Further, several thermodynamics parameters like $\Delta S°$, $\Delta H°$ and $\Delta G°$ were predicted. The value of $\Delta G°$ predicted at different temperatures, highlighted the spontaneity.

Conclusion: Dalbergia proved as a low cost and efficient adsorbent.

Keywords: Adsorption, Dalbergia, Nickel ion, Cadmium ion, Heavy metals.

INTRODUCTION

In the 21 st century, pollution has been one of the major issues concerned to environmental health. Almost every industrial sector such as steel and textile industry, automobile sectors, electroplating, mining, paint industry, petrochemical sectors and pharmaceuticals and nuclear medicine plants, tanneries etc is playing a great role in it.[1,2] All wastes of industrial sectors flow in the lakes and rivers which make unhealthy environment for flora and fauna. This waste contains various heavy

[*]**Corresponding author:** Chemical Engineering Dept., Deenbandhu Chhotu Ram University of Science and Technology Murthal Sonipat 131039 Haryana, India, Tel: 00919729599406, E-mail: priyankalahot@gmail.com

metals, pesticides, organic chemicals and dyes etc.

Heavy metals are relatively high dense materials which have high atomic number and high specific gravity. So far, researches revealed around 35 heavy metals but our present study is concerned only to the toxic metals ion only. All heavy metals are not toxic; among these only few are toxic if exceeds the permissible limit like Hg, Pb, Cd, Cr, As and Ni. These toxic metals are in the form of salt/ions when discharged from the industries and when these salts as effluent mix-up with natural resource water, their concentration may enter the food chain as contaminated water is used for agriculture and drinking purpose. These metal ions when consumed by humans, affect the central nervous system which damage kidney, lungs and even it becomes the cause of cancer.[3,4] For the removal of low concentrations of heavy metals from the water there are various method available like ion exchange, precipitation osmosis, ultra-filtration, electro dialysis, coagulation and adsorption.[5] Among all these available methods adsorption has been proved most efficient and reliable method for removal of these heavy metals.[6]

Aim of this study is to catch a potential and efficient and also promising low cost adsorbent for adsorption of heavy metals. Dalbergia is commonly found in north India. Properties of these Dalbergia tree seeds modified by chemical treatments give high absorption capacity as proved it a potential adsorbent.

METHODS

Test for adsorption of Cd and Ni on adsorbent derived from Dalbergia has been done. Heavy metals as cadmium sulfate hydrate and nickel (II) sulfate hexahydrate salts were used to prepare 25 ppm stock solution, separately. pH of the solution was adjusted by 0.1N HCL and 0.1N NaOH solution. All chemical were supplied by Merck. Absorbance of liquid sample was checked using UV vis spectrophotometer of RIGOL ultra 3660.

Dalbergia beans (Sheesham) were collected from around area and then dried in sunlight for 5 days and grounded in the local grinder. The fine powder was then chemically treated with concentrated H_2SO_4 in the weight ratio 1:1 for 12 h. The adsorbent was filtered and washed with double distilled water till neutral pH of wash water reached and the adsorbent so produced was heated at 500°C for 2 h in the muffle furnace.

Regarding to initial metal ion concentration as variable, other parameters fixed 5, 10, 15, 20 and 25 ppm were used with 0.2 g of adsorbent per 20 ml of solution. All tests were performed at 35°C and shaking was done by rotary shaker at 120 rpm for 2 h.

To test the optimum pH of solution, pH was adjusted by 0.1 N acid and base solution. As pH as variable from 2 to 10 and other parameters fixed then added optimum amount of adsorbent, after 2 h on determined mixing concentration.

To find out the optimum amount of adsorbent, this test was performed by adding 0.1g, 0.2g and 0.3g of adsorbent in the same concentration solution and then mixing after 2 h test was done.

Adsorbent is characterized by Fourier transform infrared spectrophotometer spectral analysis Perklin Elmer Frontier to know the major functional group responsible for adsorption of metal ions.[7]
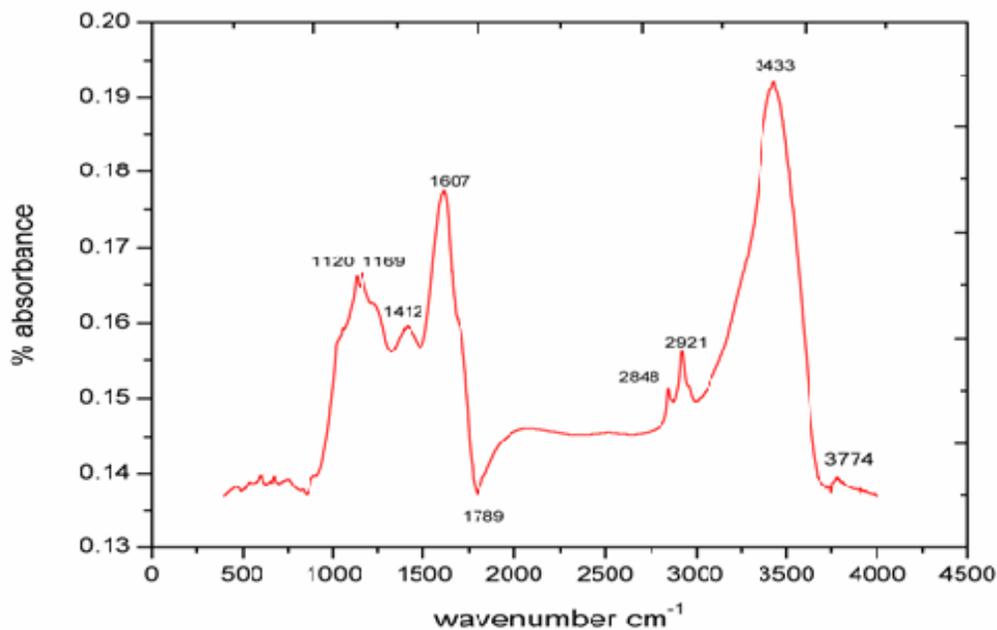
Figure 1: Infrared spectra of activated carbon prepared from Dalbergia adsorbent

The main aim of the study is to identify intensity over a different range of wavelength. The results showed a broad peak at 3433 cm^{-1} which can be attributed to-OH OR-NH groups, also band observed at 1789 cm^{-1} is due to C=O and at 2921 cm^{-1} gives stretching vibrations of saturated aliphatic of-CH.[8]

Scanning electron microscope is an instrument that assembles images of a sample by scanning it with a focused beam of electrons. This exploration shows a highly porous structure of different size and shapes. The image also shows that external surface of adsorbent is full of cavities, and indicates a high surface area and irregular in shape.[9]
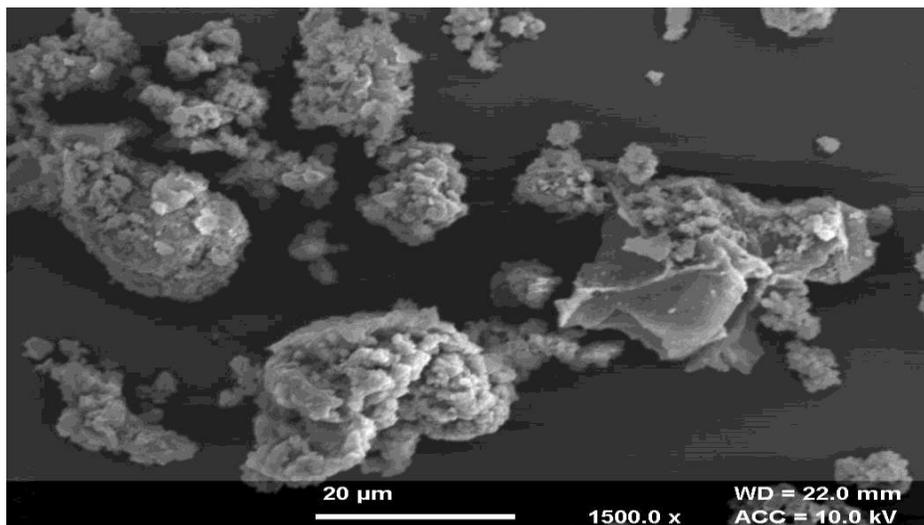

Figure 2: Scanning electron microscope micrograph of activated carbon of Dalbergia adsorbent

136

RESULTS

Adsorption theory can be explained by adsorbate and adsorbent interactions. Adsorption capacity of adsorbent can be described by equilibrium sorption isotherms, which is exactly the amount of adsorbate adsorbed on the adsorbent.[10-12]

The initial concentration provides a driving force between aqueous solution and adsorbent. After adsorption analysis, it has found that amount of metal ions adsorbed per unit mass of adsorbent is going to increase. As the percentage removal is increased amount of metal ions adsorbed is also increasing, but only upto saturation limit (5 to 15 mg/l) because no more active site present for high concentration.[13]

pH plays an important role to study the effect of adsorption capacity on metal ions. When the effect of pH is studied for Ni and Cd metal ions, initially for nickel metal ion at pH from 2 to 6, amounts adsorbed is going to decrease but later on pH from 6 to 8, amount adsorbed gives the optimum range. This is due to the acidic nature of adsorbent and point of zero net charge has important impact on exchange properties on adsorbent. When pH is less than point of zero net charge variable sites develops net positive charge or vice versa, whereas for cadmium metal ion pH when it increases, adsorption is also increased and then obtain optimum range of adsorption.
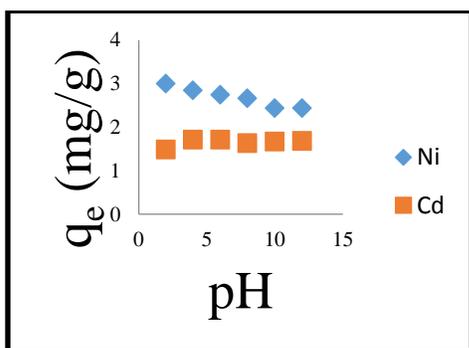
To study the effect of adsorbent dose on the adsorption capacity, experiment was conducted. When the amount of adsorbent 0.1, 0.2, and 0.3g was taken for same concentration of Ni and Cd metal ions then curve indicates the different behavior in both cases. For Ni metal ion for 0.1g and 0.2g amount adsorbed is increase at first and then, for 0.3g, it is decreased. This type of behavior indicates that the first increase in surface area as well as the binding sites but later on adsorbent actives sites are more while metal ion concentration is constant.

In the case of Cd metal ion firstly amount adsorbed is increasing due to increase in adsorbent dose, but later as increasing amount of adsorbent, amount adsorbed is going to decrease. This is due to ionic radius of cadmium ion is more as compared to the Ni ion.[14]
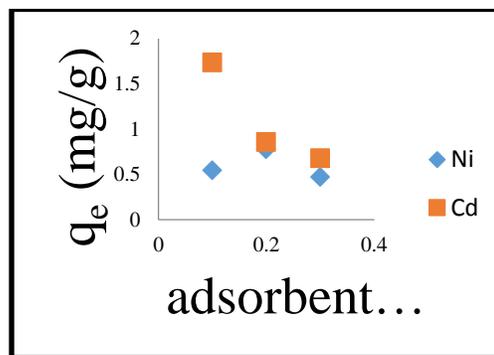

Figure 4: Effect of adsorbent quantity on adsorption of Ni and Cd

Adsorption of heavy metals on conventional adsorbents such as activated carbon has been used widely in many applications as an effective adsorbent and the activated carbon produced by carbonizing organic materials is the most widely adsorbent used.[15] Adsorption is usually described through isotherms that are amount of adsorbate on adsorbent as a

Figure 3: Effect of pH on adsorption of Ni and Cd

function of pressure and concentration at constant temperature.

Langmuir adsorption isotherm gives the information about the monolayer capacity of the adsorbent. It represents the equilibrium concentration of metal ions between the solid and liquid phases.

It is described by the following equation[13]

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{q_o \times k \times C_e}$$

Where,

C_e= Equilibrium concentration of adsorbate (mg/l^{-1})
q_e= Amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)
q_o= Monolayer capacity of the adsorbent (mg/g)
k= Langmuir adsorption isotherm constant (l/mg)

Freundlich isotherm is used to describe the adsorption characteristics for the heterogeneous surface. This data is proposed by Freundlich[16]

$q_e = K_f \times C_e^{1/n}$ linear form this equation is modified as

$\log q_e = \log k_f + 1/n \log c_e$

Where Kf= Freundlich isotherm constant (mg/g)
n= adsorption intensity
Ce= equilibrium concentration of adsorbate (mg/l)
q_e= amount of metal adsorbed per gram of the adsorbent (mg/g)

1/n is the strength of adsorption. If the value of 1/n is below 1 it indicates normal adsorption. If the value 1/n is above 1 then it is a cooperative adsorption.[17]

Temkin isotherm contains a factor that explicitly takes into the account of adsorbent-adsorbate interactions.[18] By ignoring the extremely low and large value of concentrations this model assumes that heat of adsorption of all molecules in the layer would decrease linearly rather than the logarithmic with coverage. If plot between q_e and $\ln C_e$ then this plot gives the value of slope and intercept and this slope and intercept values further gives the parameters.[19]

The equation[20] is
$$q_e = \frac{RT}{b_t} \ln(A_t C_e)$$
$$q_e = \frac{RT}{b_t} \ln A_t + \frac{RT}{b_t} \ln C_e$$
$$q_e = B \ln A_t + B \ln C_e$$
Where $B = \frac{RT}{b_t}$

A_t= Temkin isotherm equilibrium binding constant (l/g)
b_t= Temkin isotherm constant
R= universal gas constant (8.314 J/mol.K)
T= temperature (K)
B= constant related to heat of sorption (J/mol)

Langmuir fit and Freundlich does not give the exact fit with respect to R^2 values for temperature 35, 45, and 55°C. Whereas Temkin isotherm gives the best fit with respect to parameters equilibrium binding constant as increased from 0.238 to 0.376 with corresponding temperatures value as well as correlation coefficient is also increased from 0.90 to 0.96. Temkin isotherm constant (b_t) also gives positive value for both metal ions. These isotherm runs were performed for two metal ion and for three temperatures at same concentration by using magnetic stirrer for 2 h.
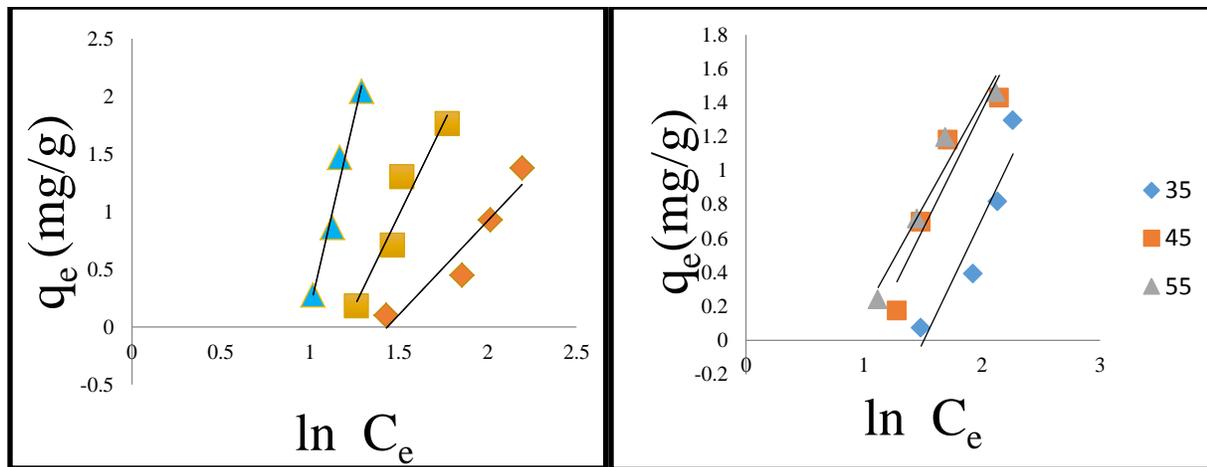
Figure 5: Temkin isotherm plot of effect of initial metal ion concentration on adsorption
(a) Ni and (b) Cd metal ions at different temperatures 35°C 45°C 55°C.

Table 1: Effect of temperature on the adsorption of Ni ion and Cd ion

	Isotherm	Langmuir	Freundlich			Temkin		
Temperature		R^2	R^2	n	B	A_T	b_t	R^2
Ni ion	35	0.961	0.992	0.283	1.629	0.238	1394.08	0.906
	45	0.780	0.842	0.226	3.172	0.303	715.94	0.928
	55	0.805	0.899	0.135	6.641	0.376	341.96	0.965
Cd ion	35	0.960	0.999	0.272	1.454	0.221	1561.87	0.876
	45	0.683	0.724	0.462	1.401	0.356	1620.96	0.886
	55	0.850	0.854	0.564	1.250	0.419	1816.77	0.949

Kinetics shows the adsorption effect with time variation or how fast the adsorption takes place and also tells s order of the reaction. So to investigate the mechanism of adsorption, pseudo first order, pseudo second order, intra-particle diffusion and Elovich kinetic models were used.

Langergren pseudo- first order rate equation is given by

$\log (q_e - q_t) = \log q_e - (k_1/2.303)t$

Where qe and qt are the amounts of metal ions adsorbed (mg/g) on adsorbent at equilibrium and at time t and k_1 is rate constant of pseudo first order adsorption (min^{-1}). Plot between $\log (q_e-q_t)$ and t shows that the adsorption of metal ions Ni and Cd on the adsorbent does not follow first order kinetics.[16,21] Rapid uptake at initial stage of adsorption is because of more number of active sites that are present on surface of adsorbent.

The langergren pseudo second order kinetic model is given as

$$t/q_t= 1/(k_2 q_e^2) + t/q_e$$

Where k_2 is rate constant of second order adsorption (g/mg.min). Slopes and intercepts of plot of t/qt vs t, is used to find out q_e and K_2. All are parameters are presented in Table.[22]
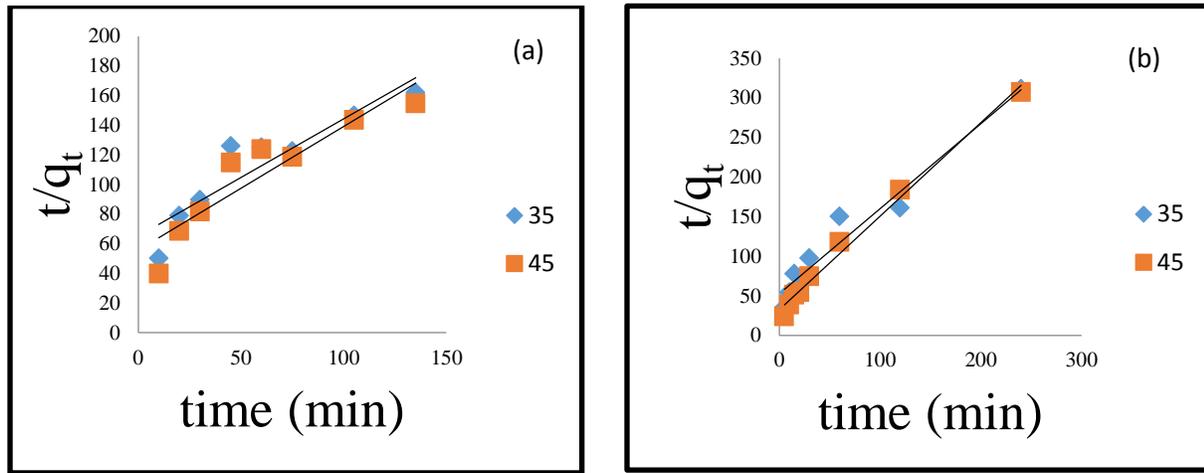

Figure 6: Pseudo second order plot of effect of contact time on adsorption
(a) Ni and (b) Cd at temperatures 35°C and 45°C.

Pseudo second order plot for cadmium ion results linear straight line with respect to R^2 values from 0.957 and 0.989 at temperature 35 and 45°C that is approximately equal to 1 which indicates the well fit and indicate that adsorption of metals ion onto adsorbent under study are of second order kinetics. The process appears to be controlled by chemisorptions which is a rate determining step. Also for nickel metal ion, qe calculated 1.199 and 1.265 which shows high adsorption capacity as for increased temperature.

Linearized form of Bhattacharya and Venkobachar first order kinetic equation is as

$$\log [1- U(t)]= -(k/2.303)t$$

Where

$$U(t)= [(C_o-C_e)/(C_o-C_e)]$$

C_e = equilibrium concentration (mg/l)

K= first order adsorption rate constant (min^{-1})

These two parameters is calculated by plotting between time and $\log [1-U(t)]$. Parameters obtained upon plotting do not give sufficient information, but it does not give fit for this adsorbent.[23]

As explained by intra-particle diffusion model $q_t= K_i \times t^{0.5}$

Where K_i intra diffusion rate constant $(mg/g^{-1} min^{-1/2})$

This is evaluated by plotting between q_t and $t^{0.5}$ represents multi linearity and this shows a

linear relationship for the whole time range but they do not cross the origin due to boundary effect. Higher values of K_i 0.08 and 0.068 shows

high rate of adsorption with high correlation coefficient 0.876 and 0.959. This equation is also well fitted in the form of linear.
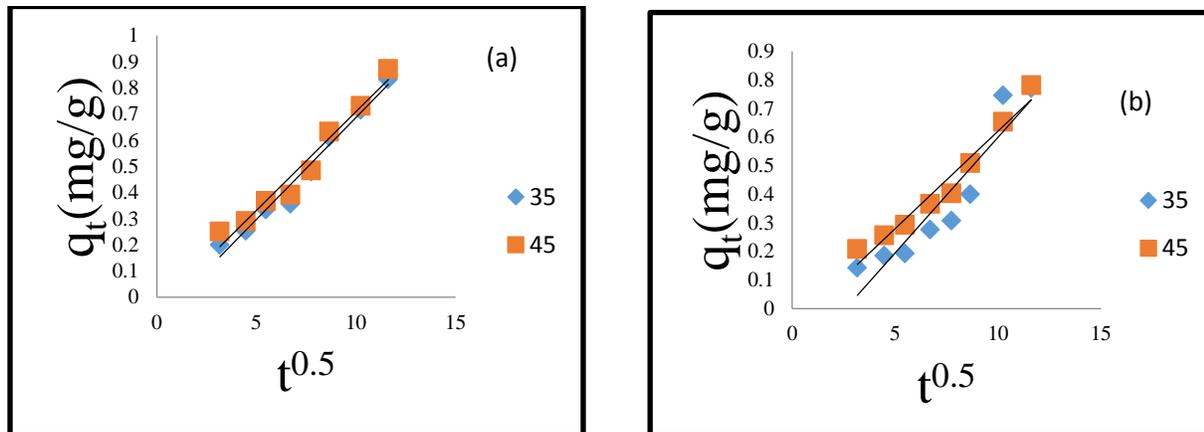

Figure 7: Intra particle diffusion plot of contact time on adsorption
(a) Ni (b) Cd at temperatures 35°C and 45°C.

Elovich kinetic equation is given by
$$q_t = 1/\beta \ [\ln (\alpha\beta)] + \ln t/\beta$$
Where α and β are constants and evaluated by slope and intercept values. Plot between q_t and $\ln t$ gives linear relation and indicates that this model used to describe second order kinetic. Constant α depends on initial rate of adsorption and result presents it is increased from 0.0251 to 0.0359,

whereas β is a desorption constant also increased 4.065 and 4.716 with temperature for cadmium metal ion. Whereas for nickel metal ion α results decrease in value with increase in R^2 values 0.80 to 0.859. Linearity shows that it gives the best fit and shows that actual solid surface is energetically heterogeneous. All the parameters calculated are placed in Table.
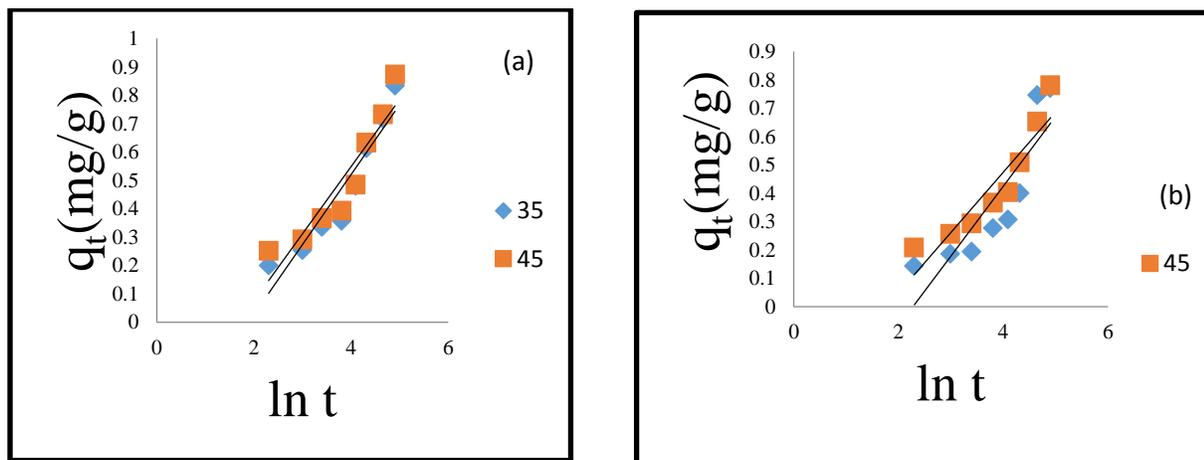

Figure 8: Elovich plot of effect of contact time on adsorption
(a) Ni (b) Cd at temperatures 35°C and 45°C.

Table 2: Effect of contact time on adsorption of Cd and Ni ion (Salman, Temel, Turan, and Ardali, 2015)

Model Temperature		Pseudo second order				Weber Morris		Elovich		
		R^2	q_e	h	K_2	R^2	K	α	β	R^2
Ni ion	35	0.957	0.932	0.0143	0.0164	0.876	0.080	0.0251	4.065	0.705
	45	0.989	0.848	0.0157	0.0219	0.959	0.068	0.0359	4.716	0.856
Cd ion	35	0.853	1.199	0.0371	0.0258	0.961	0.075	0.0430	4.237	0.805
	45	0.851	1.265	0.0245	0.0245	0.973	0.078	0.0370	4.665	0.859

In an effort to understand the nature of the process for cadmium and nickel adsorption, the thermodynamic parameter Gibbs free energy was calculated using equation

$$\Delta G° = -RT \ln K_o$$

$K_o = (C_o - C_e)/C_e$ is equilibrium constant. The Gibbs free energy change is also related by enthalpy change and entropy change. The values of Gibbs free energy change at temperatures 308, 318, 328 K is found to be -845.09, -1590.49, -2616.14 cal/mol and also shows its negative values of the reaction.[25] The negative value of Gibbs free energy change $\Delta G°$ (cal/mol) -845.09, -612.05 for 308 K and -1590.49, -1531.90 for 318 K shows the spontaneity of the reaction in case of Ni and Cd ion.[21]

DISCUSSION

Batch study reveals the results to optimum value for all parameters as initial metal ion concentration, pH effect and adsorbent dosage and also gives high adsorption capacity corresponding with regression coefficient values.

Equilibrium study results concluded that Langmuir and Freundlich isotherm does not fit although they give high correlation coefficient value rather than this negative value of intercept does not allow calculating respected constant values. Only Temkin isotherm well explained the mechanism of adsorption and constant gives positive values with respect to binding constant and heat of adsorption values. These positive and increased values of these parameters reveal that it is a physical process.

Kinetic study describes the behaviour of process and efficiency of adsorbent. Kinetic study fitted into few models out of which only pseudo second order gives quite linear relationship and decides the order of reaction also chemisorptions controlled process. Intra particle diffusion reveals that how fast diffusion takes place and results concluded that due to boundary layer effect curves points do not cross origin in fact larger the intercept decides the contribution of surface in adsorption. Elovich model concluded positive value of initial rate of adsorption and desorption constant with respect to temperatures.

Thermodynamic studies reveal that spontaneity of process. A positive value of Enthalpy change indicates the endothermic behavior of adsorption.

CONCLUSION

Adsorption is affected by all parameters and also all experiments give optimal value for each parameter. Isotherm data on

adsorbent can be modelled by Temkin isotherm giving best fit equilibrium data. Kinetics behavior is explained by Pseudo second order equation, Intraparticle diffusion and Elovich equation. Present study proved the potential of Dalbergia as a low cost adsorbent for heavy metal removal. Thermodynamic study also proves spontaneity of the reaction.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interests.

ACKNOWLEDGEMENT

REFERENCES

1. Krol M, Matras E, Mozgawa W. Sorption of Cd^{2+} ions onto zeolite synthesized from perlite waste. Int J Environ Sci Technol. 2016; 13(11): 2697-704.

2. Frutos I, Garcia-Delgado C, Garate A, Eymar E. Biosorption of heavy metals by organic carbon from spent mushroom substrates and their raw materials. Int J Environ Sci Technol. 2016; 13(11): 2713-20.

3. Varank G, Demir A, Bilgili MS, Top S, Sekman E, Yazici S, et al. Equilibrium and kinetic studies on the removal of heavy metal ions with natural low-cost adsorbents. Environ Prot Eng. 2014; 40(3): 43-61.

4. Mousavi H, Hosseynifar A, Jahed V, Dehghani S. Removal of lead from aqueous solution using waste tire rubber ash as an adsorbent. Braz J Chem Eng. 2010; 27(1): 79-87.

5. Chand P, Pakade YB. Removal of Pb from water by adsorption on apple pomace: Equilibrium, kinetics, and thermodynamics studies. J Chem. 2013; 59(8): 1-8.

6. Sharma S, Pant K, Tiwari D. Batch adsorption studies for malachite green dye removal from waste water using biomass based adsorbent. Russian J Chem. 2016; 8(2): 51-60.

7. Wang XS, Miao HH, He W, Shen HL. Competitive adsorption of Pb (II), Cu (II), and Cd (II) ions on wheat-residue derived black carbon. J Chem Eng Data. 2011; 56(3): 444-9.

8. Edokpayi JN, Odiyo JO, Msagati TA, Popoola EO. A Novel Approach for the removal of lead (II) ion from wastewater using mucilaginous leaves of diceriocaryum eriocarpum plant. Sustainability. 2015; 7(10): 14026-41.

9. Mousavi H, Hosseynifar A, Jahed V, Dehghani S. Removal of lead from aqueous solution using waste tire rubber ash as an adsorbent. Braz J Chem Eng. 2010; 27(1): 79-87.

10. Nebagha KC, Ziat K, Rghioui L, Khayet M, Naji A, Saidi M. Adsorptive removal of copper (II) from aqueous solutions using low cost Moroccan adsorbent. Part II: Kinetic and equilibrium studies. J Mater Environ Sci. 2015; 6(10): 2694-702.

11. Bulgariu L, Cojocaru C, Robu B, Macoveanu M. Eqilibrium isotherms studies for sorption of Lead ions from aqueous solutions using romanian Peat Sorbent. Environ Eng Manag J. 2007; 6(5): 425-30.

12. El Hassouni H, Abdellaoui D, El Hani S, Bengueddour R. Biosorption of cadmium (II) and copper (II) from aqueous solution using red alga (Osmundea pinnatifida) biomass. J Mater Environ Sci. 2014; 5: 967-74.

13. Patil S, Renukdas S, Patel N. Kinetic and thermodynamic study of removal of Ni (II) ions from aqueous solution using low cost adsorbents. Int J Environ Sci. 2012; 3(1): 322-40.

14. Etorki AM, El-Rais M, Mahabbis MT, Moussa NM. Removal of some heavy metals from wastewater by using of fava beans. Amer J Anal Chem. 2014; 56(9): 1-10.

15. Alam OEA, Reiad NA, Elshafei MM. A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. Int J Adv Res. 2011; 2(4): 297-303.

16. Edokpayi JN, Odiyo JO, Msagati TA, Popoola EO. A novel approach for the removal of lead (II) ion from wastewater using mucilaginous leaves of diceriocaryum eriocarpum plant. Sustainability. 2015; 7(10): 14026-41.

17. Mohan SV, Karthikeyan J. Removal of lignin and tannin colour from aqueous solution by adsorption onto activated charcoal. Environ Pollut. 1997; 97(1): 183-7.

18. Olalekan A, Dada A, Okewale A. Comparative Adsorption Isotherm Study of the Removal of Pb^{2+} and Zn^{2+} Onto Agricultural Waste. Res J Chem Env Sci. 2013; 1(5): 22-7.

19. Dada A, Olalekan A, Olatunya A, Dada O. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. J Appl Chem. 2012; 3(1): 38-45.

20. Aharoni C, Ungarish M. Kinetics of activated chemisorption. Part 2-Theoretical models. J Chem Soc Perkin Trans. 1977; 73: 456-64.

21. Bulut Y. Removal of heavy metals from aqueous solution by sawdust adsorption. J Environ Sci. 2007; 19(2): 160-6.

22. Ugurlu M, Kula I, Karaoglu MH, Arslan Y. Removal of Ni (II) ions from aqueous solutions using activated-carbon prepared from olive stone by ZnCl2 activation. Environ Prog Sustain Energy. 2009; 28(4): 547-57.

23. Ahamed AJ, Begum AS. Adsorption of copper from aqueous solution using low-cost adsorbent. Arch Appl Sci Res. 2012; 4(3): 1532-9.

24. Salman T, Temel FA, Turan NG, Ardali Y. Adsorption of lead (II) ions onto diatomite from aqueous solutions: Mechanism, isotherm and kinetic studies. Global NEST J. 2015; 17(6): 1-10.

25. Maiti A, DasGupta S, Basu JK, De S. Batch and column study: adsorption of arsenate using untreated laterite as adsorbent. Ind Eng Chem Res. 2008; 47(5): 1620-9.