Batch Adsorption Studies for the Removal of Cu (II) Ions by ZeoliteNaX from Aqueous Stream

Pankaj Pandey, S S Sambi, S K Sharma, Surinder Singh*

Abstract— The critical parameters affecting the adsorption of Cu (II) ions are investigated by utilizing ZeoliteNaX as the potential adsorbent. The adsorption of Cu(II) is strongly dependent on pH, temperature, contact time and initial adsorbate concentration. The equilibrium sorption isotherms are analyzed by the Langmuir and the Freundlich isotherms. The pH is varied from 3 to 8 and the optimum pH for Cu(II) removal is found out to be 6.0. The removal of Cu(II) ions increases with time and attains saturation in about 60-120 min. The equilibrium data shows the endothermic nature of adsorption. The thermodynamic parameters are obtained from the equilibrium data. Kinetics data show that at higher temperatures, the rate of adsorption is higher for ZeoliteNaX. Kinetics studies show that Lagergren equation successfully describes the adsorption process.

Key words: Adsorption isotherms, Cu (II), ZeoliteNaX, Kinetics, Thermodynamics

I. INTRODUCTION

Removal of Heavy metal ions from industrial and municipal wastewaters is a matter of serious concern due to their toxicity to various life forms. High intake of copper (over 1.0 mg/l in drinking water) gets accumulated in the liver of human beings and animals resulting in ailments like hemochromatosis and gastrointestinal problems [1]. It is highly toxic to fish even in small amounts and act as toxins to aquatic and terrestrial organisms [2]. A wide range of methods are available for the removal of metal ions from aqueous solutions. These include ion exchange, solvent extraction, reverse osmosis, precipitation, chemical oxidation and reduction, filtration, electrochemical treatment and adsorption. The adsorption process has been the most frequently applied method in the industries, and still is the most widely studied.

Industrial waste streams of metal cleaning, plating baths, mining, printed circuits, metallurgical, pulp and paper, fertilizers, petroleum refining, wood preserving and excessive use of Cu based agri-chemicals cause the contamination of water and soil due to copper as an toxin and carcinogen [3].

Copper along with arsenic and mercury, is recognized as the highest relative mammalian toxic species and continued inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers [4-6]. Copper sulphate is used widely as an algicide in ornamental ponds and even in water supply reservoirs, which are affected by blooms of blue green algae [7].

A number of researchers have utilised wide variety of adsorbents to remove heavy metal ions from aqueous solutions. Some of the recent developments include adsorbents like herbaceous peat[1], carbon aerogel[3], iron-oxide coated sand[4], sawdust[6], ca-kaolinite[7], Fithian illite[8], fly ash[9], baggase[10], activated carbon-zeolite composite [11], zeolite A [12], fertilizer plant waste slurry [13], modified clay [14], biosorbents like cassava waste [15], Areca [16] etc. for the removal of copper ions from aqueous solutions.

Zeolites are crystalline alumino-silicates having uniform cavities and having strong ion-exchange capacity. The substitution of aluminium for silicon results in a residual negative charge density, which is balanced by the presence of other metallic ions in the pores of the framework. Due to their structural characteristics, zeolites can be used in several applications [18]. Zamzow et.al. [19] used clinoptilolite to remove Al, Fe, Cu, and Zn from copper mine wastewater. Ouki and Kavannagh [20] investigated that clinoptilolite and chabazite differ in their performance regarding capacity and selectivity. Biserka Biškup et.al.[12] studied the exchange processes between the sodium ions from zeoliteNaA and cadmium, copper and nickel ions from solutions.

The process of removal of metal ions takes place in Zeolite by two steps i.e. adsorption and by ion exchange process [17] [21]. For ion exchange process the removal of heavy metals from solution is based on the factors like: Type of counter ion to be exchanged, Size of the pore opening in Zeolite, Ion exchange equilibrium between aqueous solution and ZeoliteNaX [22] [23].

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II. MATERIALS AND METHODS

Adsorbent: ZeoliteNaX (purchased from CDH, India) is used in this work for the removal of copper ions from aqueous solutions. ZeoliteNaX is in the form of cylindrical pellets with 1.5 mm diameter and having 20% binder. In order to obtain, as far as possible, the homo-ionic sodium form, the ZeoliteNaX as received is contacted three times with 1 molar solution of NaCl at room temperature. It is then washed with HPLC grade ultrapure water, oven dried at 373 K and stored over saturated ammonium Chloride.

Chemicals and reagents

Chemicals used for all the experiments are of Analytical and Lab Reagents grades. HPLC grade ultrapure water is used in all experiments.

Copper Ion Stock Solution: Stock solution of 1000 mg/l Cu(II) ion is prepared dissolving copper sulphate pentahydrate ($CuSO_4.5H_2O$) purchased from MERK India Ltd in water. To do this 3.772gm $CuSO_4.5H_2O$ is added in HPLC grade ultrapure water contained in 1000ml volumetric flask.

Buffer preparation:

Different pH buffers have been used over a range of 3-8 to study the effect of pH on the removal efficiency of the adsorbent. For maximum range of pH, solution of Acetic acid and Sodium Acetate are used for maintaining the pH of the solution.

III. EXPERIMENT

Equilibrium studies:

Batch equilibrium experiments have been carried out to find the optimum pH, contact time and equilibrium isotherms. A series of 250 ml conical flask are used. The procedure involved filling each flask with 250 ml of copper ions solution of 25 ppm. ZeoliteNaX is added into different flasks kept 24 hours in shaking incubator to achieve equilibrium. The effect of pH for copper ions removal using ZeoliteNaX is studied in a pH range of 3 to 8. The amount of ZeoliteNaX is varied from 0.5 to 2gm.

Batch Kinetic Studies:

Batch kinetic experiments are carried out to find kinetics of the adsorption process. 500 ml conical flasks are employed. The procedure involved filling conical flask with 250 ml of 5-25 mg/l Cu (II) ion solution. The solution is adjusted to optimum pH 6.0 and 2g ZeoliteNaX is added. During the experiment small amount of samples are taken for analysis at predetermined intervals.

Analysis:

The Cu (II) ions in the solution are analyzed using atomic adsorption spectrophotometer purchased from ECIL India which operates in flame mode.

IV. RESULTS AND DISCUSSION

1. Effect of pH

The mechanism of adsorption at the ZeoliteNaX surface reflects the nature of physicochemical interaction of the metal ions in the solution and the active sites of the ZeoliteNaX. The pH is varied from 3 to 8 during this study. The effect of pH on the removal of copper ions by ZeoliteNaX is found to be significant as shown in Figure1. The uptake capacity of ZeoliteNaX is found maximum at pH 6.0. It can be seen from the Figure1 that the removal of metal ions is strongly dependent on the pH of the solution. But pH less than 4.5 is not recommended for Zeolites [24]. The loss in removal capacity at lower pH can therefore be attributed to the collapse of the structure of zeolites [17].

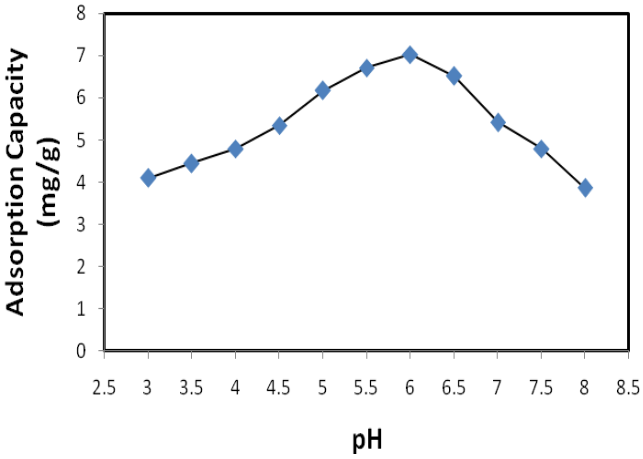

Figure1: Effect of pH on adsorption of Cu (II) onto ZeoliteNaX at 288±1K

2. Effect of temperature

Effect of temperature on adsorption of Cu(II) ions is studied by conducting different sets of experiments at initial concentration of 25 ppm at different temperatures i.e. 288, 303, 323^o K and as shown in Figure2. It is observed that adsorption of Copper ions increases with increase in the temperature.

3. Effect of contact time

The effect of contact time and different initial concentrations is also studied. It is observed that percentage removal of Cu (II) ions decreases with increase in initial metal concentration. The removal of Cu (II) increases with time and attains saturation in 60to 120 min. The removal rate of adsorption is rapid initially but it gradually decreases with time until it reaches equilibrium. The Figure3 shows the change in effluent concentration with respect to time. It is observed that remaining concentration of metal ions becomes asymptotic to the time axis after a definite interval of time and no further adsorption takes place in the batch experiments.

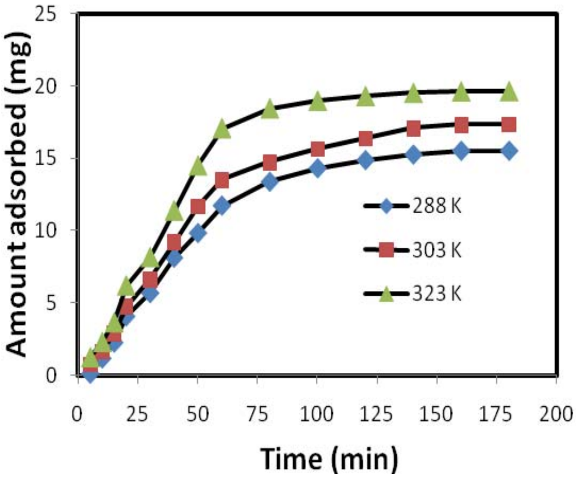

Figure2: Effect of Temp on adsorption of Cu (II)

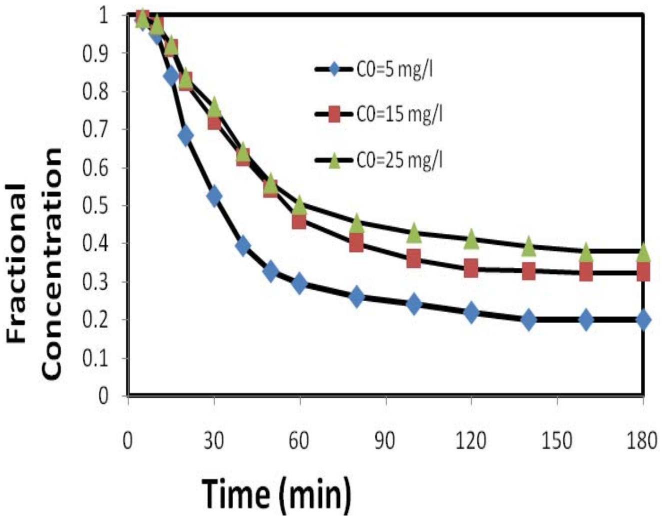

Figure3: Effect of contact time on Adsorption of Cu

4. 1 Adsorption Isotherms

The adsorption isotherms are studied using initial concentration of Cu (II) between 5 and 25 mg/L at an adsorbent dose of 2gm/L. The data obtained is fitted into the Langmuir adsorption isotherm which is the most popular and is a two-parameter equation described as:

$$\frac{C_e}{q_e}=\frac{1}{q_m b}+\frac{C_e}{q_m} \qquad \text{-------} \quad \mathbf{(1)}$$

Where constants b and q_m relate to the energy of adsorption and adsorption capacity and their values are obtained from the slope and intercept of the plot of Ce/qe versus Ce as shown in Figure4 for temperature 288K. The linear nature of the plot shows that the adsorption follows the Langmuir isotherm. The value of b, which is a measure of heat of adsorption is utilized to calculate dimensionless separation parameter R_L [29]. The adsorption data obtained are also fitted to the Freundlich isotherm which is the earliest known relationship known as described by the following equation:

$$\log q_e = \log K + \frac{1}{n}\log C_e \qquad \mathbf{(2)}$$

where K and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity respectively. The slope (1/n) and intercept (K) of a log-log plot of qe versus C_e are determined. The results of both regressed isotherms are tabulated in Table I. The results show that both isotherms well fit the experimental data as shown in Figure 4.

4.2. Thermodynamic parameters

The thermodynamic equilibrium constant (K_C) is obtained by calculating the apparent equilibrium constant K'_C at different initial concentrations of Cu(II) and extrapolating to Zero. [27]

$$Kc' = \frac{Ca}{Ce} \qquad \mathbf{(3)}$$

Where C_a is the concentration of Cu (II) on the adsorbent at equilibrium in mg/L and C_e is the equilibrium concentration of Cu (II) in solution in mg/L. The thermodynamic constants, Gibb's free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) are calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. The Gibb's free energy change of the process is related to equilibrium constant (K_c) by equation 4 as below:

$$\mathbf{\Delta G^0 = - RT \ln K_C} \qquad \mathbf{(4)}$$

The Gibb's free energy change is related to the enthalpy change (ΔH°) and entropy change (ΔS°) as:

$$\mathbf{\ln K_C = \Delta S0/ R - \Delta H^0/ RT} \qquad \mathbf{(5)}$$

The parameters as calculated are also reported in Table II. The negative ΔG° value confirmed the feasibility of the sorption process and the spontaneous nature of adsorption. The positive value of ΔH° obtained indicated the endothermic nature of the process. The positive ΔS° value indicated the affinity of the adsorbent for Cu (II).

Weber and Chakarborti [29] expressed the essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant separation factor $R_{L,}$ which is defined as:

$$R_L = \frac{1}{1+b\text{Co}} \qquad \mathbf{(6)}$$

where b is the Langmuir constant and C_0 is the initial concentration of Cu (II). According to McKay et.al [30] R_L values between 0 and 1 indicate favorable adsorption. The data obtained represent a favorable adsorption in the case of adsorption of Cu (II) ions (R_L = 0.102). The shape of isotherm is given by the value of R_L as given in Table II.

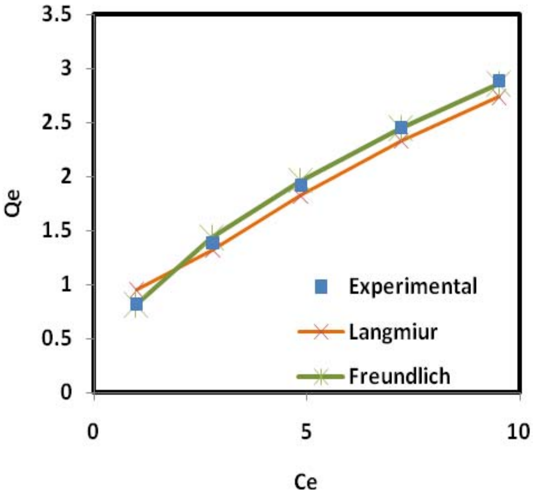

Fig 4: Experimental and predicted values of Isotherm plot for adsorption of Cu 288(±1) °K and at pH 6.0

Table I. Estimated parameters for Cu(II) adsorption at 288 K and at pH6.0

Isotherm Models	Estimated isotherm parameters		
Langmuir Equation $\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$	R^2	Q_m (mg/g)	b (L/mg)
	0.952	41.6	0.353
Freundlich Equation $\log q_e = \log K + \frac{1}{n} \log C_e$	R^2	K (mg/g)	n
	0.998	0.81	1.785
Thermodynamic parameters evaluated	ΔG (kJ/mol) -1.049	ΔH (kJ/mol) 17	ΔS (kJ/mol K) 0.626

Table II:

(Separation Factor R_L)

R_L Value	Type of isotherm	R_L (Obtained)
$R_L > 1$	Unfavorable	-
$R_L = 1$	Linear	-
$0 < R_L < 1$	Favorable	0.102
$R_L = 0$	Irreversible	-

TABLE III: Kinetic Models and other statistical parameters at 288^{0}K and pH 6.0

Kinetic model	**Parameters**	**Concentration of Ni(II)**		
		(5 mg/l)	**(15 mg/l)**	**(25 mg/l)**
1st order equation $-\ln(C/Co) = K_1 t$	R^2	0.804	0.866	0.877
	K_1	0.009	0.007	0.006
2nd order equation $1/C - 1/Co = K_2 t$	R^2	0.915	0.947	0.933
	K_2	0.005	0.001	0.000
Lagergren equation $\log(q_e - q) = \log q_e - (K_r/2.303)t$	R^2	**0.980**	**0.978**	**0.992**
	K_r	**0.032**	**0.035**	**0.028**
Pseudo second order $1/(qe-q) = 1/qe + K_{2'} t$	R^2	0.811	0.624	0.903
	$K_{2'}$	0.076	0.041	0.009
Power function equation $\text{Log } q = \log a + b \log t$	R^2	0.786	0.860	0.855
	a	0.044	0.0674	0.0724
	b	0. 986	1.079	1.179

5. Adsorption kinetics

The time-dependent experimental adsorption data are used for kinetic modeling. The model equations used for fitting the data are:

- 1st order equation
- Pseudo 1st order model (Lagergren equation)
- Second order equation
- Pseudo 2nd order equation
- Power function equation

The present Cu (II)-sorption data of ZeoliteNaX at 288±1K and pH 6.0 are tested for kinetic modelling by linear regression plots. The estimated models and the related statistical parameters are reported in Table III (graphs are not shown). Based on linear regression (R^2>0.975) values, the kinetics of Cu (II) adsorption onto ZeoliteNaX was best described by Lagergren equation (R^2= 0.992). The results clearly indicate that the pseudo first order function (Lagergren) model fits progressively well with increasing sorbate concentration.

V. INTRAPARTICLE DIFFUSION

Besides adsorption at the outer surface there is also possibility of intraparticle diffusion from the outer surface into the pores of the material. The adsorption mechanism of a sorbate onto the adsorbent follows three steps viz. film diffusion, pore diffusion and intraparticle transport.[28] Though there is a high possibility for pore diffusion to be the rate-limiting step in a batch process, the adsorption rate parameter which controls the batch process for most of the contact time is the intraparticle diffusion[25][26]. Thus to evaluate the rate controlling step a plot was drawn between amount of Copper adsorbed on ZeoliteNaX vs. $(\text{time})^{1/2}$ as shown in Fig. 7. The first part of the curve is attributed to mass transfer effects (slope K_1) taking place with boundary layer diffusion, while the final linear parts indicate intraparticle diffusion (slope K_2 and K_3). The diffusion rate parameters K_1, K_2 and K_3 as obtained are shown in Table IV. The values for K_2 and K_3 indicate that the pores are micro-pores and the intraparticle diffusional resistance is due to micro-pores only [17]. The diffusion rate parameters indicate that the intraparticle diffusion controls the sorption rate; which is the slowest step in adsorption. Moreover, sorption of Cu (II) in pores of ZeoliteNaX is concentration dependent. Increase in sorbate concentration increases the rate of pore diffusion.

TABLE IV: Macro- and micro-pore diffusion rate constants

Adsorbate concentration (mg/ℓ)	Rate constants, Intraparticle rate parameter (mg/g·$min^{0.5}$)		
	K_1	**K_2**	**K_3**
15 mg/l	0.766	0.244	0.102
25mg/l	1.209	0.322	0.021

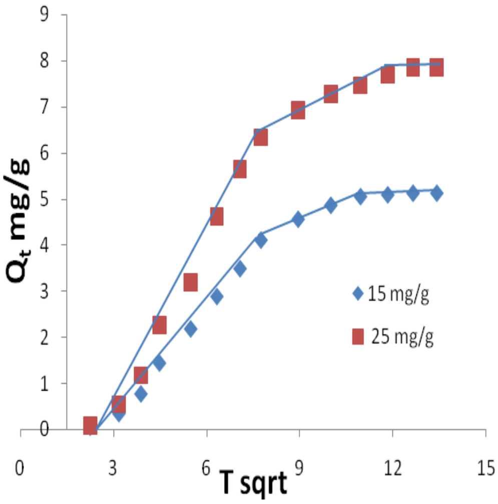

Fig: 7 Intraparticle and pore diffusion plots for Adsorption of Cu (II) at 288(±1)°K and at pH 6.0

VI. CONCLUSIONS

- The calculated values of the dimensionless separation factor R_L from the Langmuir isotherm constants confirm favorable sorption of Cu (II) onto ZeoliteNaX.
- Optimum pH for highest Cu(II) adsorption is 6.0
- The thermodynamic calculations showed that the Cu (II) adsorption was spontaneous in nature and endothermic nature of the adsorption process.
- The contact time for the maximum adsorption required is nearly 90 mins.
- Adsorption process is found to follow the first order Lagregren rate kinetics.
- Before exploiting the recovery of heavy metals commercially using ZeoliteNaX and its application in both batch and packed columns, the pilot scale studies should be carried out in detail.

REFERENCES

[1] Recep Gündo˘gan et.al.; Copper (II) adsorption from aqueous solution by herbaceous peat, Journal of Colloid and Interface Science Vol. 269, 2004 pp. 303–309.
[2] R.T. Camp, Water and its Impurities, 2nd edition, Reinhold , New York, 1964.
[3] Ajay Kumar Meena et al.; Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, Journal of Hazardous Materials Vol B122, 2005, pp. 161–170.
[4] N. Boujelben et.al; Adsorption of nickel and copper onto natural iron oxide-coated sand from aqueous solutions: Study in single and binary systems, Journal of Hazardous Materials vol. 163, 2009, pp. 376–382.
[5] H.J.M. Bowen, The Environmental Chemistry of the Elements, Academic Press, London, 1979.
[6] S.R. Shukla, Roshan S.Pai, Adsorption of Cu(II), Ni (II) and Zn(II) on dye loaded groundnut shells and sawdust, separation and purification Technology, Vol. 43, 2005, pp. 1-8.
[7] M. Doula, A. Ioannou, A. Dimirkou,

Thermodynamics of copper adsorption -desorption by ca-kaolinite, Adsorption Vol.6, 2000, pp 325–335.

[8] Xueyuan Gu, Les J.Evans, Modelling the adsorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) onto Fithian illite Journal of Colloid and Interface Science Vol. 307, 2007 pp. 317–325.

[9] Panday, K. K.; Prasad, G.; Singh, V. N.; Copper (II) removal from aqueous solutions by fly ash, Wat. *Res*. Vol.19, 1985, pp.869.

[10] Aly HM, Daifullah AAM; Potential use of bagasse pith for the treatment of wastewater containing metals, *Adsorp Sci Technol*, vol.16, 1998,pp.33–38.

[11] Vinay Kumar Jha et.al.;Sorption properties of the activated carbon-zeolite composite prepared from coal fly ash for Ni2+, Cu2+, Cd2+ and Pb2+, Journal of Hazardous Materials, Vol 160, 2008, pp. 143-153.

[12] Biserka Biškup, Boris Suboti; Kinetic analysis of the exchange processes between sodium ions from zeolite A and cadmium, copper and nickel ions from solutions; *Separation and Purification Technology*, vol.37, 2004 pp. 17–31.

[13] Srivastava SK, Tyagi R, Pant N. Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plants. *Wat Res,* vol. 23, 1989, pp.1161–5.

[14] T. Vengris, R. Binkiene˙, A. Sveikauskaite; Nickel, copper and zinc removal from waste water by a modified clay sorbent; *Applied Clay Science* vol.18, 2001,pp.183–190.

[15] A.A. Abia et al.; The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution, Bioresource Technology Vol. 90 , 2003, pp. 345–348.

[16] Wei zheng et al.; Adsorptive removal of Cadmium and copper from aqueous solution by areca- a food waste Journal of Hazardous Materials Vol 157, 2008, pp. 490–495.

[17] Surinder Singh et. al.; Adsorption Behaviour of Ni (II) from Water onto Zeolite X: Kinetics and Equilibrium Studies, Proceedings of the World Congress on Engineering and Computer Science 2008 WCECS 2008, October 22 - 24, 2008, San Francisco, USA, ISBN: 978-988-98671-0-2.

[18] Pansini M.; Natural zeolites as cation exchangers for environmental protection, *Miner Deposita*, vol. 31, 1996, pp.563–75.

[19] Zamzow MJ, Eichbaum BR, Sandgreen KR, Shanks DE; Removal of heavy metals and other cations from wastewater using zeolites. *Sep Sci Technol,* vol. 25, 1990, pp.1555–69.

[20] Ouki SK, Kavannagh M.; Treatment of metal contaminated wastewaters by use of natural zeolites, *Water Sci Technol*, vol.39, 1999, pp.115–22.

[21] Dyer, H.et-al; The plotting and interpretation of ion-exchange isotherms in charcoal systems**, Sep**. *Sci. Technol***.**, vol.16, 1981,pp.173-183.

[22] Blanchard G., Removal of heavy metals from waters by means of natural zeolites, *Water Res.*, vol.18, 1984, pp.1501-1507.

[23] Curkovic S.; Metal ion exchange by natural and modified zeolites; *Wat. Res.,* vol.31, 1997, pp.1379-1382.

[24] Biskup, B.et-al.; Removal of heavy metal ions from solutions using zeolite: influence of sodium ion concentration in the liquid phase on the kinetics of exchange processes between cadmium ions from solution and sodium ion from Zeolite A: *Sep. Sci. and Tech.*, vol.39, 2004, pp.925-940.

[25] Allen Sj, Mckay G And Khader Khy ;(1989) Intraparticle diffusion of basic dye during adsorption onto Sphagnum Peat, *J. Environ. Pollut.* Vol.50**,** 1989, pp.39-50

[26] Weber Wj (Jr.) and Morris Jc.;(1963) Kinetics Of Adsorption on Carbon from solutions. *J. Sanit. Div. Am. Soc. Civ. Eng*., vol. 89**,** 1963, pp. 319.

[27] A K Bhattacharya et.al.; Adsorption of Zn(II) from aqueous solution by using different adsorbents. Chemical engineering Journal Vol. 123, 2006 pp.43-51.

[28] Pant K. K., Singh T. S., Equilibrium, kinetics, and thermodynamics, study for adsorption of As (III) ions on activated alumina, *Separation and purification technology,* vol. 36, 2004, pp.139-147.

[29] T.W. Weber, R.K. Chakraborti, Pore and solid diffusion models for fixed bed adsorbents, J. AIChE 20 (1974) 228–238.

[30] G. McKay, H.S. Blair, J.R. Gardener, Adsorption of dyes on chitin. I. Equilibrium studies, J. Appl. Polym. Sci. 27 (1982) 3043–3057.