Adsorption Behaviour of Ni (II) from Water onto Zeolite X: Kinetics and Equilibrium Studies

Surinder Singh, Lokesh Kumar Verma, S S Sambi, S K Sharma

Abstract— The optimal parameters affecting the adsorption of nickel ions, Ni (II) on Zeolite X are determined. The adsorption of Ni (II) is strongly dependent on pH, temperature and initial adsorbate concentration. The equilibrium adsorption data follow the Langmuir and the Freundlich isotherms. The maximum adsorption capacity of Zeolite X is estimated to be 46mg/g. The optimum pH for Ni (II) removal is found out to be 5.2. The equilibrium data show 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 Zeolite X. Kinetics studies show that Lagergren, and second order equations successfully describe the adsorption process.

Key words: Zeolite X, Adsorption, Nickel, Kinetics

I. INTRODUCTION

The presence of trace metals in the aquatic environment has been of great concern because of their toxicity and non-biodegradable nature. Nickel is toxic and relatively widespread in the environment. It is used in a wide variety of industries such as plating and cadmium–nickel battery, phosphate fertilizers, mining, pigments, stabilizers and alloys, and find its way to the aquatic environment through wastewater discharge. Therefore, a systematic study on the removal of nickel from wastewater is of considerable significance from an environmental point of view. A number of methods are available for the removal of metal ions from aqueous solutions. These are ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption. Adsorption process has been and actually is the most frequently applied method in the industries, and consequently the most extensively studied. A number of workers have used different adsorbents viz. pea nut shells [1], walnut shells [2], bone [3], automobile tires [5], Gypsum [6], activated carbon [7] [8] baggase [9][10], soya cake [11], blast furnace slag [12], Fly ash [13], fertilizer plant waste slurry [14], activated carbon from olive pulp [15], perlite [16] etc., developed from various waste materials for the removal of heavy metals. There is still a need to develop low cost and efficient adsorbents for the removal of nickel from wastewater.

T. Vengris et. al. [17] used modified natural clays by treating with hydrochloric acid and subsequent neutralization of the resultant solution by sodium hydroxide for removal of nickel, copper and zinc and found that the uptake capacity of the modified clay for nickel, copper and zinc did significantly increase. A.H. Elshazly [18] et al. studied the removal of nickel ions from wastewater polluted with nickel chloride using a cation-exchange resin in a stirred tank reactor. Their results revealed that the use of a strong cation-exchange resin in a stirred tank reactor for nickel ion removal is a promising technique for wastewater treatment in view of the fact that rate of nickel ion removal up to 88.5% were obtained.

A three-dimensional tetrahedral framework characterizes zeolites. 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. These metallic ions are, typically, hydrated alkali and alkaline earth cations, which are exchangeable. The sub-nanometric size of the channels acts as a molecular sieve, by hindering the passage or allocation of bigger chemical species. Due to their structural characteristics, zeolites can be used in several applications [19]. For example Zamzow et. al. [20] used clinoptilolite to remove Al, Fe, Cu, and Zn from copper mine wastewater to below drinking water standards. Concerning the removal of heavy metals from mixed aqueous solutions, Ouki and Kavannagh [21] showed that clinoptilolite and chabazite differ in their performance regarding capacity and selectivity. Biserka Biškup et. al. [22] studied the exchange processes between the sodium ions from zeolite A and cadmium, copper and nickel ions from solutions and concluded that the process could be modeled by the second order forward and backward chemical reactions.

First author Surinder Singh is with the DeenBandhu Chhotu Ram University of Science and Technology, Murthal, Sonepat, Pin-131039, Haryana, India.
He is Lecturer in Department of Chemical Engineering.
(Phone: 91-9416874644, 91-9215874644; fax: 91-130-2484004; e-mail: sonu_unos@yahoo.co.in, sonubhinder@gmail.com).
Second author. Lokesh Kumar Verma was Research Scholar with University School of Chemical Technology, Guru Gobind Singh Indraprastha University, Kashmiri Gate, and Delhi, India.
Third Author Dr S S Sambhi is with the University School of Chemical Technology, Guru Gobind Singh Indraprastha University, Kashmiri Gate Delhi. He is presently Dean of School of Chemical Technology at GGS Indraprastha University, Delhi, India.
Fourth author Dr S K Sharma is Lecturer with University School of Chemical Technology Guru Gobind Singh Indraprastha University, Kashmiri Gate, and Delhi, India.

The removal of metal ions takes place in Zeolite in two steps i.e., by adsorption and by ion exchange process [23] [24]. For ion exchange process the removal of heavy metals from solution is based on several factors like: Type of counter ion to be exchanged, Size of the pore opening in Zeolite, Ion exchange equilibrium in aqueous solution and Ion Exchange of Zeolite-X [25] [26].

The aim of the present study is to evaluate exchange behavior of Zeolite-X for removal of Nickel from wastewater in batch process. In this work the effect of pH, temperature and sorbent concentration on adsorption capacity has been studied and equilibrium, thermodynamic and kinetic model parameters have been evaluated

II. MATERIALS AND METHODS

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

Chemicals and reagents

Chemicals used for the experiments are of AR and LR grades. Double distilled water is used for all experiments.

Nickel Ions Solution: $NiSO_4.6H_2O$ purchased from MERK is in the form of green color crystals. To make the synthetic solution of nickel sulphate, say of 100 mg/l, 447.9 mg of nickel sulphate is added in 1000 ml distilled water contained in 1000ml volumetric flask.

Buffer preparation:

Different pH buffers have been used over a range of 3-7 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. Experimental

Equilibrium studies:

Batch equilibrium experiments have been carried out to find the optimum pH, and equilibrium isotherms. A series of 250 ml conical flask are employed. The procedure involved filling each flask with 250 ml of Ni ions solution of 100 ppm. About 1g zeolite is added into different flasks and stirred intermittently for four hours and then flasks have been sealed and kept as such for 24 hours so that equilibrium can be achieved. The effect of pH for nickel ions removal using zeolite is studied in a pH range of 3 to 7. The amount of zeolite is varied from 0.5 to 2 gms.

Batch Kinetic Studies:

Batch equilibrium experiments are carried out to find kinetics of adsorption. A 250 ml conical flask is employed. The procedure involved filling flask with 250 ml of Ni ions solution of 100 ppm. The Ni^{2+} solution is adjusted to the optimum pH 5.3 and optimum adsorbent 1 g zeolite.

Analysis: The Ni ion in solution is analyzed using Atomic adsorption spectrophotometer make ECIL, India in flame mode.

IV. RESULTS AND DISCUSSION

1. Effect of pH

The mechanism of adsorption at the zeolite surface reflects the nature of physicochemical interaction of the metal ions in the solution and the active sites of the Zeolite. The pH is varied from 2 to 7 during study. The effect of pH on the removal of nickel ions by zeolite is found to be significant as shown in Fig.1. The uptake capacity of zeolite is found maximum at pH of 5.2. It can be seen from the figure that the removal of metal ions is dependent on the pH of the solution.

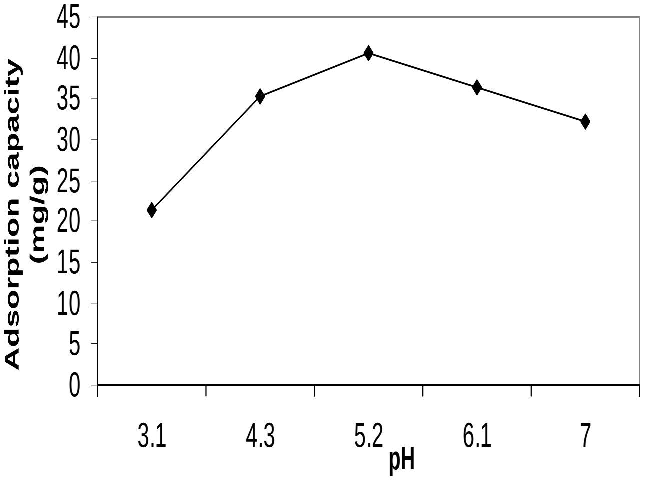

Fig 1: Effect of pH on adsorption of Ni (II) onto Zeolite at 303(±1)°K

The structure of zeolites, particularly with low Si/Al ratio may collapse in the presence of acids with pH lower than 4, but the severity will be more at pH below 3. In fact, pH less than 4.5 is not recommended for Zeolite [27]. The loss in removal capacity at lower pH can therefore be described to the collapse of the structure of zeolites.

2. Effect of temperature

Different sets of experiments are conducted at different concentrations starting from 25 ppm to 125 ppm at different temperatures at 293, 303, 313° K and it is evident in the Fig.2 that adsorption of Nickel increases with increase in the temperature.

3. Effect of amount of adsorbent

The effect of amount of adsorbent on the uptake of nickel, at the optimum pH is examined. Nickel ion removed versus amount of zeolite shows that the removal of metal ions increases with an increase in the amount of zeolite. For nickel there is a substantial increase when the dose of zeolite is increased from 2 gm to 3.5gm, and then the increase in the removal efficiency is not so significant when the zeolite amount is further increased as could be seen from the Fig.3. The value of uptake for zeolite is 46mg Ni (II) per gm of zeolite.

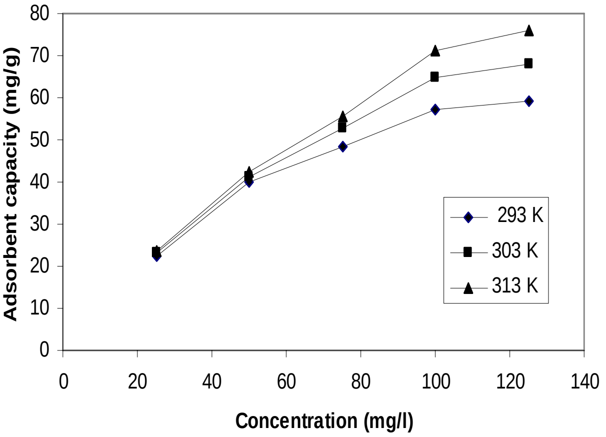

Fig 2*:* Effect of Temp on adsorption of Ni

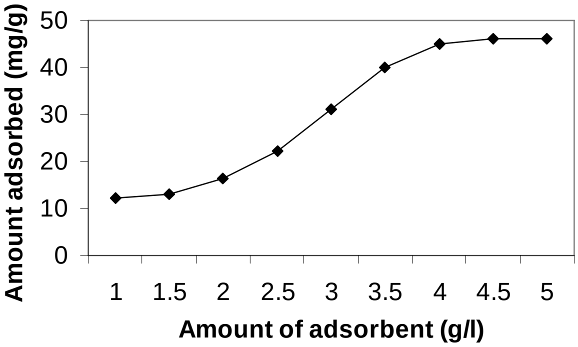

Fig 3: Effect of amount of adsorbent on Adsorption of Ni

4. Adsorption Isotherms

Adsorption isotherm data are quantified to describe the interactions between the adsorbate and adsorbent and are critical in optimizing the use of adsorbent [10]. The Langmuir equation is the most popular of all the nonlinear isotherm expressions; it is a two-parameter equation:

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

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 Fig 5 for temperature303 K. The linear nature of the plot shows that the adsorption follows the Langmuir isotherm and increase in temperature from 293 to 313 K resulted in an increase of about 24 % in adsorption capacity (Table II). The value of b, which is a measure of heat of adsorption, decreased slightly with an increase in temperature. The Freundlich isotherm equation for representing equilibrium data is given by:

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

Where K and n are Freundlich constants 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 (Fig 6) as determined are tabulated in Table II. An increase in temperature resulted in an increase in K indicating increased adsorption capacity.

The thermodynamic constants, Gibb’s free energy (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) 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 3 as below:

$$\mathbf{\Delta G^0 = - RT \ln K_O} \qquad \mathbf{(3)}$$

The Gibb’s free energy change is related to the enthalpy change (ΔH^o) and entropy change (ΔS^o) as:

$$\mathbf{\ln K_O = \Delta S^0 / R - \Delta H^0 / RT} \qquad \mathbf{(4)}$$

Where Ko is equilibrium constant (m3mol-1) that is calculated from the Langmuir constant b [28]. The values of enthalpy change (ΔH^o) and entropy change (ΔS^o) are calculated from the slope and intercept of the plot of ln K_c versus 1/T (Fig. 4). The parameters as calculated are also reported in Table II. The negative ΔG^o value confirmed the feasibility of the sorption process and the spontaneous nature of adsorption. The positive value of ΔH^o obtained indicated the endothermic nature of the process. The positive ΔS^o value indicated the affinity of the adsorbent for Ni (II).

5. Adsorption kinetics

The time-dependent experimental adsorption data are used for kinetic modelling. 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

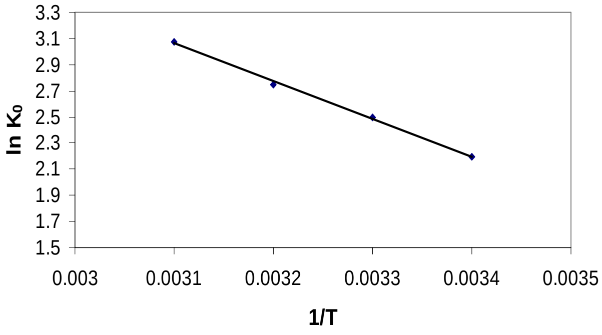

Fig 4: Estimation of thermodynamic parameters at pH 5.2

TABLE I. Adsorption isotherm and thermodynamic parameters

Temperature (K)	*Langmuir Isotherm constant* b (L/mg)	q$_m$ (mg/g)	R^2	*Freundlich isotherm constant* K (mg/g)	n	R^2	-ΔG° (*kJ mol^{-1}*)	ΔH° (*kJ mol^{-1}*)	ΔS° (*kJ mol-1 K^{-1}*)
293	0.168	64	0.996	18.3	3.38	0.967	5.35	24	0.100
303	0.157	74	0.992	19.3	3.07	0.987	7.15		
313	0.156	84	0.985	20.7	2.89	0.989	8.26		

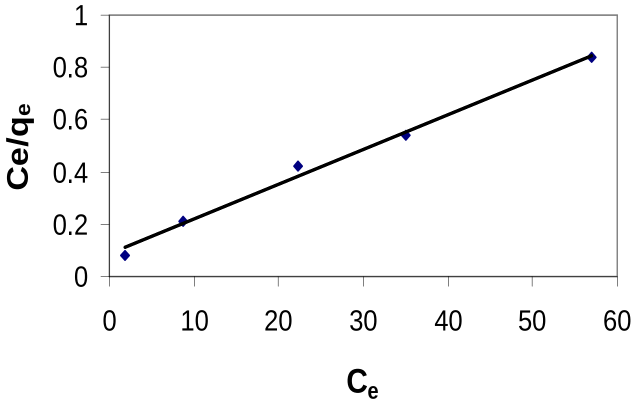

Fig 5: Langmuir isotherm plot for adsorption of Ni at 303(±1)°K and at pH 5.2

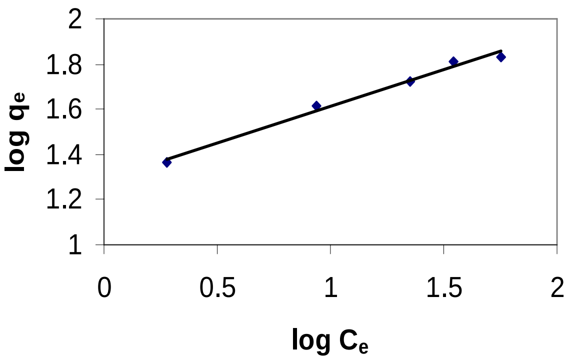

Fig 6: Freundlich isotherm plot for adsorption of Ni at 303(±1)°K and at pH 5.2

TABLE II: Kinetic Models and other statistical parameters at 303^{0}K and pH 5.2

Kinetic model	**Parameters**	**Concentration of Ni(II)**		
		(25 mg/l)	**(50 mg/l)**	**(100 mg/l)**
1st order equation	R^2	0.916	0.9326	0.8813
-ln(C/ Co) = K$_1$t	K$_1$	1.05*10^{-2}	8.1*10^{-3}	7.2*10^{-3}
2nd order equation	R^2	0.9729	0.9893	0.9746
1/C- 1/ Co = K$_2$t	K$_2$	1.5*10^{-3}	4.0*10^{-4}	2.0*10^{-4}
Lagergren equation	R^2	0.9770	0.9791	0.9891
log(q$_e$-q)=log q$_e$ - (K$_r$/2.303)t	K$_r$	6.4*10^{-2}	2.4*10^{-2}	3.29*10^{-2}
Pseudo second order	R^2	0.7179	0.6021	0.5737
1/ (qe-q) = 1/ qe+ K$_{2'}$t	K$_{2'}$	1.52*10^{-2}	1.24*10^{-2}	2.11*10^{-2}
Power function equation	R^2	0.9596	0.9542	0.9789
Log q = log a + b log t	a	1.066	0.3158	0.2965
	b	0.139	1.0062	1.1572

The present Ni (II)-sorption data of zeolite at 303 (±1)°K and pH 5.2 are tested for kinetic modelling by linear regression plots. The estimated model and the related statistic parameters are reported in Table III (graphs are not shown). Based on linear regression (R^2>0.95) values, the kinetics of Ni (II) adsorption onto zeolite could be described well by both Lagergren equation (R^2= 0.9770, and second order equation (R^2= 0.9729). The results clearly indicate that the power function model fits progressively well with increasing sorbate concentration

V. MACRO AND MICRO-PORE DIFFUSION

The adsorption mechanism of a sorbate onto the adsorbent follows three steps viz. film diffusion, pore diffusion and intraparticle transport. The slowest of these steps controls the overall rate of the process. Generally, pore diffusion and intraparticle diffusion are rate-limiting in a batch reactor, while for a continuous flow system film diffusion is more likely to be the rate-limiting step [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[29][30]. Thus to evaluate the rate controlling step plot was drawn between amount of nickel adsorbed on zeolite vs. $(\text{time})^{1/2}$ as shown in Fig.7. The first part of the curve is attributed to mass transfer effects (slope K1) taking place with boundary layer diffusion, while the final linear parts indicate intraparticle diffusion (slope K2 and K3). The diffusion rate parameters K1, K2 and K3 as obtained are shown in Table 5. The values for K2 and K3 indicate that the pores are micro-pores and the intraparticle diffusional resistance is due to micro-pores only. The diffusion rate parameters indicate that the intraparticle diffusion controls the sorption rate; which is the slowest step in adsorption. Moreover, sorption of Ni (II) in pores of zeolite is concentration dependent. Increase in sorbate concentration increases the rate of pore diffusion.

TABLE III: 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**
25 mg/l	0.544	0.377	$8.26*10^{-2}$
50mg/l	1.003	0.504	$8.71*10^{-2}$

VI. CONCLUSIONS

- The calculated values of the dimensionless separation factor from the Langmuir isotherm constants confirm favorable sorption of Ni (II) onto Zeolite.
- The study shows that Zeolite-X is a better alternative to activated carbon for metallic waste treatment.
- Regeneration studies for metal recovery and its application in packed column should be studied in detail before its commercial exploitation.

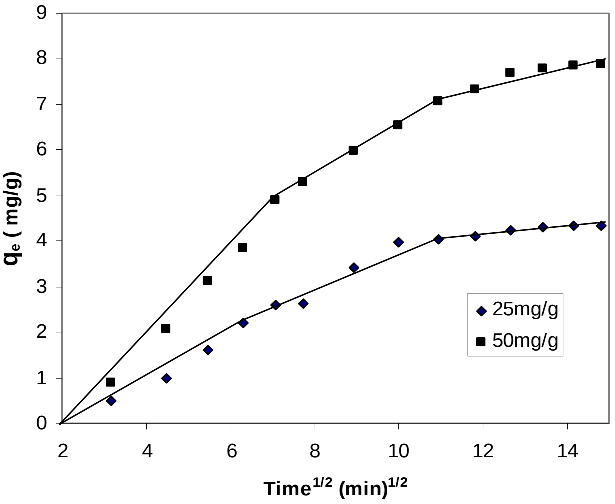

Fig: 7 Intraparticle and pore diffusion plots for Adsorption of Ni (II) at 303(±1)°K and at pH 5.2

References

[1] Apak, R.; Tutem, E.; Hugul, M.; Hizal; Heavy metal cation retention by unconventional sorbent (red mud and fly ashes), J. *Wat. Res*. Vol.32, 1998, pp.430.

[2] Banerjee, K.; Cheremisinoff, P. N.; Cheng, S. L; Adsorption kinetics of o-xylene by fly-ash *Wat. Res*. Vol.31, 1997,pp.249.

[3] Danis, T. G.; Albanis, T. A.; Petrakis, D. E.; Pomonis, P.J.; Removal of heavy metal mesoporous alumina aluminum phosphates *Wat. Res*. Vol.32, 1998, pp.295.

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

[5] Williams, C. J.; Aderhold, D.; Edyvean, R. G.; Novel biosorbents for the removal of metals from aqueous effluents, *Wat. Res*. Vol. 32, 1998, pp.216.

[6] Baltpurvins, K. A.; Burns, R. C.; Lawrance, G. A.; Stuart, A. D.; Effect of electrolyte composition on zinc hydroxide precipitation by lime. *Wat. Res*. Vol.31, 1997, pp.973.

[7] J.R. Rangel-Mendez, M. Streat; Adsorption of cadmium by activated carbon cloth: Influence of surface oxidation and solution pH, *Water Research*, vol.36, 2002, pp. 1244–1252.

[8] Halil Hasar; Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from almond husk, *Journal of Hazardous Materials,* Vol.97B, 2003, pp. 49–57.

[9] 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.

[10] Vinod K. Gupta, C.K. Jain, Imran Ali, M. Sharma, V.K. Saini Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste *Water Research*, vol. 37, 2003, pp.4038–4044

[11] Daneshvar N, Salari D, Aber S. Chromium adsorption and Cr (VI) reduction to trivalent chromium in aqueous solutions by soya cake. *J Hazardous Mater*, vol.94B, 2002, pp.49–61.

[12] Dimitrova SV, Mehandgiev DR. Lead removal from aqueous solution by granulated blast furnace slag. *Wat Res,* vol.32, 1998, pp.3289–92.

[13] Ferraiolo G, Zilli M, Converti A.; Fly ash disposal and utilization, *J Chem. Techno Biotechno* , vol. 47, 1990; pp.281–306.

[14] 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.

[15] Galiatsatou P, Metaxas M, Kasselouri-Rigopoulou V. Adsorption of zinc by activated carbon prepared from solvent extracted olive pulp, *J Hazardous Mater,* vol. B91, 2002, pp.187–203.

[16] Mathialagan T, Viraraghavan T. Adsorption of cadmium from aqueous solutions by perlite. *J Hazardous Mater*, vol. B94, 2002, pp.291–303.

[17] 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.

[18] A.H. Elshazly, A.H. Konsowa; Removal of nickel ions Corn wastewater using a cation-exchange resin in a batch-stirred tank reactor; *Desalination*, vol. 158, 2003, pp.189-193

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

[20] 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.

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

[22] 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, 2004pp. 17–31.

[23] Ahmed, S. C., Keane; The removal of cadmium and lead from aqueous solution by ion exchange with Na-Y charcoal; *Sep. and Pur. Tech*., vol.13, 1998, pp.57-64.

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

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

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

[27] 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.

[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] 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

[30] 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.