Removal of Cu^{2+}, Pb^{2+}, And Ni^{2+} Ions From Simulated Waste Water By Ion Exchange Method On Zeolite And Purolite C105 Resin

Dr. Ahmed Abed Mohammed **Haidar Shukur Mahmood**

Baghdad University/College of Eng.
Environmental Engineering Dept.
ahmed.abedm@yahoo.com

ABSTRACT:

The removal of heavy metal ions from wastewater by ion exchange resins (zeolite and purolite C105), was investigated. The adsorption process, which is pH dependent, shows maximum removal of metal ions at pH 6 and 7 for zeolite and purolite C105 for initial metal ion concentrations of 50-250 mg/l, with resin dose of 0.25-3 g. The maximum ion exchange capacity was found to be 9.74, 9.23 and 9.71 mg/g for Cu^{2+}, Pb^{2+}, and Ni^{2+} on zeolite respectively, while on purolite C105 the maximum ion exchange capacity was found to be 9.64 ,8.73 and 9.39 for Cu^{2+}, Pb^{2+}, and Ni^{2+} respectively. The maximum removal was 97-98% for Cu^{2+} and Ni^{2+} and 92-93% for Pb^{2+} on zeolite, while it was 93-94% for Cu^{2+}, 96-97% for Ni^{2+}, and 87-88% for Pb^{2+} on purolite C105. The obtained sorption affinity sequence was $Cu^{2+} > Ni^{2+} > Pb^{2+}$ in both resins. Langmuir isotherm expressions were found to give better fit to the experimental data compared to Freundlich and BET models. Kinetic data correlated well with Lagergren first order kinetic model, indicating the reversible reaction with an equilibrium being established between liquid and solid phase.

KEYWORDS: ion exchange, heavy metals, wastewater, zeolite, purolite C105.

ازاله ايونات النحاس، الرصاص والنيكل من المياه الملوثه بطريقه التبادل الايوني باستخدام راتنجات الزيولايت والبيورلايت

احمد عبد محمد **حيدر شكر محمود**

الخلاصه:

ازالة المعادن الثقيلة من مياه الصرف الصحي بواسطة راتنجات التبادل الايوني، مثل الزيولايت و البيورولايت تمت دراستها بطريقة الدفعة. ، والتي تعتمد على الدالة الهيدروجينية ، يظهر الحد الأقصى لإزالة ايونات المعادن في درجة الحموضة بين 6 و 7 للزيولايت والبيورولايت لتركيز المعادن الأولية للايونات 50-250 ملغم / لتر ، مع جرعة من الراتنج من 0.25 الى 3 وتم التوصل إلى توازن في ساعتين. تم ايجاد السعة القصوى للتبادل الايوني لتكون 9.74ملغ /غ للنحاس، 9.23ملغ /غ للرصاص و 9.71ملغ /غ للنيكل على راتنج الزيولايت بينما على راتنج البيورولايت السعة القصوى للتبادل الايوني كانت 9.64ملغ /غ للنحاس 8.73ملغ /غ للرصاص و 9.39ملغ /غ للنيكل .وان نسبه الازالة القصوى كانت 97- 98% للنحاس و النيكل و حوالي 92-93% للرصاص على راتنج الزيولايت في حين كانت نسبة الازالة القصوى على راتنج البيورولايت حوالي
93 -97 % للنحاس و النيكل و 87-88% للرصاص. تم ايجاد ان تعبير لانكمير هو الملائم اكثر لتمثيل هذه البيانات المختبرية مقارنة بفريندلخ و بي اي تي . البيانات الحركية تبين انها ملائمة مع الدرجة الاولى، مشيرة الى ان التفاعل عكسي مع التوازن الذي يجري بين السائل و المادة الصلبة .

1. INTRODUCTION

Heavy metals are generally considered to be those whose density exceeds 5 g/cm^3 (Nocito et al.,2007). Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies but they are also toxic to many life forms. Industrial processes generate wastewater containing heavy metal contaminants. Since most of heavy metals are non degradable into nontoxic end products, their concentrations must be reduced to acceptable levels before discharging them into the environment. Otherwise they could pose threats to public health and/or affect the aesthetic quality of potable water (Aslam et al.,2004).

According to World Health Organization (WHO) the metals of most immediate concern are chromium, copper, zinc, iron, nickel, mercury and lead (WHO, 1984). The removal of heavy metal cations from aqueous solutions can be achieved by several processes, such as chemical precipitation, biosorption on marine algae, adsorption, solvent extraction, reduction, coagulation, oxidation, reverse osmosis, flotation, ultra filtration and ion exchange (Keane,1998; Rengaraj et al.,2004)

The most common method used for the removal of these heavy metals is ion exchange. The main advantages of ion exchange are recovery of metal value, cost-effective, selectivity and the meeting of strict discharge specifications. In ion exchange systems, polymeric resins are usually employed. The resin is a very complex material and there are several properties which are to be known and clearly understood before putting it to any particular application. Some of the important properties are: moisture content, particle size, cross linking, resin capacity, functional groups, resin selectivity, and distribution coefficient. In ion exchange, ions of positive and negative charges from an aqueous solution replace dissimilar ions of the same charge initially in the solid. The ion exchangers contain permanently bound functional groups of opposite charge type. Cation exchange resins generally contain bound sulfonic acid groups, carboxylic acid groups phosphonic acid groups, phosphinic acid groups and so on (Pehlivan and Altun,2006).Using Zeolite as an ion exchange for environmental protection and other applications is stimulated by the good results obtained, the non toxic nature of these materials, their availability in many parts of the worlds, and the low cost (Campos et al.,2007). Removal and recuperation processes of heavy metals from aqueous solution by natural zeolite are commonly cyclic and take into account the recovery of the metals and the regeneration of the zeolite to be reused.

Additionally, the mineral stability of zeolites and their structural changes under treatment in various media play important roles in their potential utilization as ion exchangers (Sprynskyya et al.,2006)

Weak cation acid(WAC) resins have very high selectivity for divalent cations, particularly Pb^{2+}, Cu^{2+}, $Cd^{2+,}$ and Ni^{2+} ions. This makes them ideal candidates for the removal of various metals from wastewater streams. WAC resins offer extremely high capacity than strong cation resins, higher selectivity for divalent cations than chelating resins, especially at neutral to alkaline pH, have relatively low cost, and have lower kinetics, compared to chelating resins (Pehlivan and Altum,2007)

Ion exchange reaction is reversible interchange between solid phase (the ion exchange) and the solution phase, the ion exchanger being insoluble in the medium in which the exchange is carried out. If an ion exchanger $M^-A^{+,}$ carrying cations A^+ as the exchanger ions, is placed in an aqueous solution phase containing B^+ cations, an ion exchange reaction takes place which may be represented by the following equation:

$$M^-A^+ + B^+ \longleftrightarrow M^-B^+ + A^+ \quad .....(1)$$

The equilibrium represented by the above equation is an example of cation exchange, where M^- is the insoluble fixed anionic complement of ion exchanger M^-A^+, often called simply the fixed anion. The cations A^+ and B^+ are referred to counter- ions .whilst ions in the solution which bear the same charge as the fixed ion of the exchanger are called co-ions. In much the same way, anions can be exchanged provided that an anion-receptive medium is employed. An analogous representation of an anion exchange reaction may be written:

$$M^+A^- + B^- \longleftrightarrow M^+B^- + A^- \quad .....(2)$$

The equations above illustrate the essential difference between ion exchange and other sorption phenomena (Harland 1994).

The aim of the present work is to study the removal of Cu^{2+}, Pb^{2+}, and Ni^{2+} from industrial waste water by ion exchange method using zeolite and purolite C105 resins. In addition, investigate the parameters that influence the ion exchange, such as contact time, pH, dose of resin, and initial concentrations. The isotherms models and kinetics parameters were also evaluated from the ion exchange measurements.

2 EXPERIMENTAL WORK AND PROCEDURE

The experimental work was performed in a batch mode by using synthetic zeolite and purolite C105 resins for the removal of heavy metal ions and making comparison between these resins in order to get the most efficient resin for heavy metals removal.

2-1 Materials

Analytical grade reagents were used. Solutions of certain molarities were prepared by dilution of chloride dehydrated, nickel sulfate hexahydrate and lead nitrate salts ($CuCl_2.2H_2O$, $NiSO_4.6H_2O$ and $Pb(NO_3)_2$) from Merck company with double distilled water. Synthetic zeolite and Purolite C105 in hydrogen form UK were used, the properties of the resins are given in tables 1and 2

2-2:Apparatus.

Atomic Absorption Spectrometer: AAS was used to measure concentrations of soluble copper, lead and nickel (Norwalk, Connecticut, U.S.A). The pH measurement was performed with pH bench meter (Type: HI 250, Bench model, USA). High-speed orbital shaker has an adjustable shaking range of 100 to 2200 rpm (Thermolyne, Maxi-Mix III, Type: 65800, USA) was used for ion exchange experiments.

2-3 Procedure

The resins were washed with 1M of NaOH and 1M HCl in order to remove possible organic impurities, then washed with distilled water to remove all excess acids and basics then dried for 24 hours.

The procedure involved filling number of flasks with 50 ml of heavy metal ions solution of 100 ppm concentration unless otherwise specified, and an amount of 0.25-3 g of adsorbent was added into different flasks. Resins and solution were mixed at 200 rpm, and then were allowed to reach equilibrium for 2 hrs in the shaker. The separation was performed using filter paper. The same measurements were repeated twice and the average value had been taken as the amount of the remaining metal in the solution phase.

3 RESULTS AND DISCUSSION

3-1 Effect of Contact Time

The effect of contact time on the ion exchange of metal ions by zeolite and purolite C105 was studied by adding 0.25 g of resin to 50 ml of metal solution in different flasks that were shaken for different time intervals. Figure (1-a) shows the effect of contact time on ion exchange of copper, lead, and nickel using zeolite, while figure (1-b) shows the effect of contact time using purolite C105. From these figures it can be seen that the percentage of metal ion sorbed increased with increasing time and it reached equilibrium at 2 hrs for zeolite and purolite C105. Further increase in contact time had no significant effect on copper, lead, and nickel removal. The kinetics of metal ions removal by the resin were relatively fast, which within 30 min uptake of 76.6% copper, 73.3% lead, 82.6% nickel on zeolite resin were achieved. While uptake on purolite C105 were 73% copper, 67.8 % lead, and 84% nickel were achieved at 30 min. The initial adsorption rate was very fast and this may be due to the existence of greater number of resin sites available for the adsorption of metal ions. As the remaining vacant surface sites decreased, the adsorption rate slowed down due to the formation of repulsive forces between the metals on the solid surface and in the liquid phase (Yua et al.,2009). The increased uptake of metal ions with contact time can be due to the decrease mass transfer coefficient of the diffusion controlled reaction between resins and metal ions. This is a crucial parameter for an optimal removal of metal ions in waste water (Zaiter,2006). The ion exchange rate was faster and the equilibrium removal efficiency was higher for copper than that of lead and nickel in zeolite resin. While in purolite C105 the ion exchange rate was faster and the equilibrium removal efficiency of nickel was higher than that of of copper and lead. The maximum removal efficiency was 99%, 94%, 98% and 94%, 93%, 98%, for copper, lead and nickel, on zeolite and purolite C105 respectively.

3-2 Effect of pH

pH affects both the surface charge of adsorbent and the degree of ionization of heavy metals in the solution (Shah et al.,2011). Equal quantity of resin 0.5 g was added to all reaction flasks and the solutions contain 100 mg/l heavy metal ions that were agitated for 2 hrs on zeolite and purolite C105 resins at 200 rpm speed. The maximum removal on zeolite were about 97%, 94%, and 96% for copper, lead, and nickel, respectively at pH ranges 5.5-8, as shown in figure (2-a) while for purolite C105 were about 92%, for copper and nickel and 91%,for lead , at pH ranges 6-9 as shown in figure (2-b). This may be attributed to the competition between hydrogen, sodium, and metal.

3-3 Effect of Resin Dose

The resin amount is an important parameter to obtain the quantitative uptake of metal ions (Rafati et al.,2010). The retention of the heavy metals was examined in the relation to the amount of resin used, 0.25 to 3 g of zeolite and purolite C105 that were tested and equilibrated for 2 hrs. The results plotted in figure (3) show that by increasing the resin amount, the sorption density, and the amount of adsorbed metal ion per unit mass increased. The retention of metals increased with increasing the amount of resin up to 0.5 g for both resins, this value was taken as the optimum amount for other trials. The increase in sorbent amount resulted in a decrease in the contact time required to reach equilibrium. The results were expected because for a fixed initial metal concentration the resin provides greater surface area or ion exchange sites or adsorption site (Gupta and Bhattacharyya,2009). It is readily understood that the number of available sorption sites increases by increasing the resin amount. It may be concluded that by increasing the adsorbent dose, the removal efficiency increases but the ion exchange density decrease .The decrease in the ion exchange density can be attributed to the fact that some of ion exchange remains unsaturated during the sorption process whereas the number of ion exchange sites increases by an increase in sorbent dose and this results in an increase in the removal efficiency (Rafati et al.,2010). The optimum dose of 0.5g was observed enough to reach high removal efficiencies.

3-4Effect of Initial Metal Concentrations

Figure (4) shows the effect of varying metal concentrations 50-250 mg/L on the adsorption under the optimized conditions. It was found that the metal amounts retained were almost stable in the concentration ranges of copper, lead, nickel, and the two types of resins. Adsorption of metal ions was a bit higher in zeolite than in purolite C105. At high concentrations the removal efficiency decreased because of the slow motion of metal ions. The maximum removal efficiency on zeolite resin was obtained as 99.4%, 97%, and 98.5% for copper, lead and nickel respectively, while the maximum removal efficiency on purolite C105 was obtained as 98%, 93%, and 97% for copper, lead, and nickel respectively for 50 mg/l initial metals concentration.

4. SORPTION ISOTHERMS

Adsorption isotherms are very powerful tools for the analysis of adsorption processes. Adsorption isotherms establish the relationship between the equilibrium pressure or concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. Langmuir, Freundlich, and BET isotherms models are widely used to investigate the adsorption process. The model parameters can be construed further, providing the understanding of adsorption mechanisms, surface properties, and affinity of the adsorbent.

4-1 Langmuir isotherm

Langmuir equation relates the coverage of molecules on a solid surface to the concentration of a medium above the solid surface at a fixed temperature. The isotherm is based on three assumptions, namely, adsorption is limited to monolayer coverage, all surface sites are alike and can only accommodate one adsorbed atom, and the ability of a molecule to be adsorbed on a given site is independent of its neighboring site's occupancy (Yua et al.,2009). The Langmuir equation was developed in the 1990s to describe the sorption of gas molecules on planer surfaces. This model was later extended to liquid systems, where species in solution are involved. The Langmuir model (Langmuir, 1916) suggests that sorption occurs on homogenous surfaces by monolayer sorption (sorption onto a surface with a finite number of identical sites), without interaction between sorbed molecules. Equation (1) describes the model

$q_e=(q_m bC_e)/(1+bC_e)$ ..... (1)

Where: b = constant related to the affinity of the binding site (L mg^{-1}),q_e = sorbed metal ions on the resin (mg g^{-1}). C_e = metal ions concentration in the solution at equilibrium (mg L^{-1}), q_m = maximum sorption capacity for a monolayer coverage (mg g^{-1}) which is the maximum sorption amount of the metal ion per unit weight of biomass needed to form a complete monolayer on the surface. q_m represents a practical limiting sorption capacity when the surfaces are fully covered with metal ions and assists in the comparison of sorption performances. The sorption parameters (q_m,b) can be determined from the linearized form by plotting Ce/qe vs. Ce according to eq (2):

$C_e/q_e = 1/(q_m\ b)+ C_e/q_m$ …..(2)

4-2 Freundlich isotherm

The Freundlich isotherm describes equilibrium on heterogeneous surfaces and hence, doesn't assume monolayer capacity and takes the following form for a single component adsorption (Freundlich,1906)

$q_e = K_F\, C_e^{1/n}$ ….. (3)

Where: K_F and n = the Freundlich constants

K_F related to the adsorption capacity, the larger its value, the higher the capacity, n is the adsorption intensity or the heterogeneity of the sorbent; the more heterogeneous the surface, the larger its value. If 1/n approaches 1, the equation becomes linear. If 1/n value within 0.1 and 1 there is a favorable sorption of the sorbate on the given sorbent. The Freundlich relation is an exponential equation that assumes that the concentration of adsorbate on the adsorbent surface increases by increasing the adsorbate concentration in the liquid phase. Equation (4) can be linearized in logarithmic form and the Freundlich constants can be determined

$\text{Log}\ q_e = (1/n) \log C_e + \log K_F$ ….. (4)

The values K_F and n can be estimated respectively from the intercept and slope of a linear plot of experimental data of log q_e versus log C_e. Freundlich isotherm provides no information on the monolayer adsorption capacity in comparison with the Langmuir model. This isotherm is widely recommended due to its accuracy. It gives more accurate results then the Langmuir isotherm for a wide variety of heterogeneous adsorption systems

4-3 BET isotherm

The BET isotherm was developed by Brauner, Emmet and Teller. Unlike the Langmuir isotherm, BET type adsorption corresponds to multilayer adsorption. This isotherm indicates that more than one layer of adsorbate can accumulate at the surface, i.e. the first adsorbed layer serves as a site for adsorption of a molecule onto the second and so on. It also supposed that the adsorption/ desorption occurs exclusively between the interface and the bulk, and the atoms are not allowed t omove from one layer to other (Masel, 1996).

The Langmuir, Freundlich, and BET adsorption constants are evaluated from isotherms and their correlation coefficients are presented in tables 3, 4 and 5. The linearized Langmuir, Freundlich, and BET of copper, lead, and nickel for zeolite and purolite resins are given in figures 5, 6, and 7. The Langmuir model constants evaluated from isotherms and their correlation coefficients are presented in table 3. Ion exchange capacity of heavy metal cations listed in table 3 indicates the following selectivity sequence: $Cu^{2+} > Ni^{2+} > Pb^{2+}$. Since the adsorption phenomena depends on the charge density of cations, the diameter of hydrate cations is very important. The charges of the metal cation are the same (+2); therefore Pb^{2+} ions (the biggest diameter) have minimum adsorption while Cu^{2+} and Ni^{2+} ions (the least diameter) have maximum adsorption. The Langmuir model effectively described the sorption data with all R^2 values > 0.97 for each resin. According to the b parameter, sorption on zeolite and purolite C105 are produced following the sequence $Cu^{2+} > Ni^{2+} > Pb^{2+}$ The Freundlich model constants k_F and n on zeolit and purolite C105 are, respectively, obtained from the intercept and the slopes of the linear plot of log q_e versus log C_e according to equation 4 and their correlation coefficients for each resin are presented in table 4.

The BET isotherm has been used to describe sorption of metal ions on ion exchange resins as shown in eq. (5):

$$\frac{X}{q_e(1-X)} = \frac{1}{ab} + \frac{(b-1)}{ab}X \text{ ….. (5)}$$

Where: $X = C_e/q_e$

The slope of the plot $X/q_e\,(1-X)$ versus X gives (b-1)/ab and the intercept yields the sorption capacity 1/ab. The plot of $X/q_e\,(1-X)$ against X for metal ion sorption on zeolite and purolite C105 are shown in figure (7) respectively. The BET parameters for zeolite and purolite C105 are listed in table 5. It is clear that the Langmuir isotherm model provide an excellent represent to the equilibrium adsorption data, giving correlation coefficients of 0.984 for copper, 0.978 for lead, and 0.982 for nickel on zeolite resin. While giving correlation coefficients of 0.970 for copper, 0.984 for lead, and 0.979 for nickel on purolite C105 resin.

5. ADSORPTION KINETICS

Kinetics of sorption describing the solute uptake rate, which is in turn governs the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption (Pehlivan and Altun,2006). Several researchers have used different kinetic models to predict the mechanism involved in the sorption process. These include pseudo-first-order model, pseudo-second-order-order model, Webber and Morris sorption kinetic model, first-order reversible reaction model, external mass transfer model, Pseudo first order and second order kinetic models are widely used [(Pehlivan and Altun,2006,2007)

5-1 Pseudo first-order kinetics

Lagergren showed that the rate of adsorption of solute on the adsorbent followed a pseudo first-order equation. The non-linear form of pseudo first-order equation is given by

$$\text{Log } (q_e-q_t) = \log q_e - K_1\, t/2.303 \text{ …..(6)}$$

Where: q_e and q_t = amounts of adsorption at equilibrium time. K_1 = rate constant of the pseudo first-order adsorption operations.

5-2 Second order kinetics

Pseudo first-order kinetic equation differs from a true first order equation in two ways: The parameters K_1 and (q_e-q_t) represent the number of available site.The parameter log $(q_e)$is an adjustable parameter and often it is not equal to the intercept of the plot of $\log(q_e-q_t)$ vs.t, whereas in a true first order log q_e should be equal to the intercept. In such cases, applicability of the second order kinetics has to be tested with the rate equation given by eq. (7):

$$t/q_t = 1/h + (1/q_e)t \text{ …..(7)}$$

Where: $h = K_2 q_e^{\,2}$

Under such circumstances, plotting log (q_e-q_t) against "t" for zeolite and purolite C105 provides the first order rate constant (k_1),while plotting t/qt vs. t should give a linear relationship, which allows the computation of pseudo second orde rate constant(K_2), q_e and b. as listed in tables 6,7,8 and 9, respectively.

The values of correlation coefficient indicate a better fit of Lagergren first order model with the experimental data than pseudo second order model. In many cases the first order kinetic process is used for reversible reaction with an equilibrium being established between liquid and solid phases. Whereas, the second order kinetic model assumes that the rate limiting step may be chemical adsorption .Values of q_e calculated from the first order kinetic model agree very well with the experimental values, and the correlation coefficients were always more than 0.97 for all metal ions and on both resins.

6. CONCLUSIONS

1-Zeolite and purolite C105 are effective resins for the removal of copper, lead, and nickel from wastewater.

2-Zeolite is a better alternative than purolite C105 for removal of metal ions from wastewater at an optimum pH of about 6 and 7 onto zeolite and purolite C105 respectively.

3-It was observed that an increase of resin dosage resulted in a higher metal ions removal efficiency and by increasing the resin dosage the contact time required to reach equilibrium decreased.

4-The linear Langmuir, Freundlich, and BET isotherms were used to represent the experimental data, and the experimental data could by relatively well interpreted by Langmuir isotherm for both resins.

5-The monolayer adsorption capacity of copper, lead, and nickel calculated from Langmuir model was obtained 9.74, 9.23 and 9.71 mg/g on zeolite resin. While on purolite C105 resin the monolayer adsorption capacity of copper, lead, and nickel was 9.64, 8.73 and 9.39 mg/g respectively.

6-The sorption of metal ions on zeolite and purolite C105 resins followed first order reversible kinetics.

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Table 1. Properties of Purolite C105.

Polymer Matrix Structure	Acrylic Crosslinked with DVB
Physical Form and Appearance	Macroporous spherical beads
Whole Bead Count	95% min.
Functional Groups	R-COOH
Ionic Form ,as shipped	H
Total Exchange Capacity, H^+ form, wet, volumetric	4.2 eq/l min
Moisture Retention, H+ form	45-52%
Particle Size Rang	+1.2 mm <5%, -0.3 mm <1%
Swelling $Na^+ \rightarrow H^+$	65% max.
Shipping Weight (approx.)	720-800 g/l
Specific Gravity, moist H^+ Form	1.18
pH Range, operating	4 - 14

Table 2. Physical properties of Zeolite pellets.

Dimension	Bulk Density	Particle Density	Void Fraction of Bed	Surface Area
2mm*2mm	0.58 g/cm^3	2.38 g/cm^3	0.3	7.82 m^2

Table 3. Langmuir isotherm for ion exchange of metal ions on zeolite and purolite C105.

Metal	Zeolite			Purolite C105		
	q_m	b	R^2	q_m	b	R^2
Cu^{2+}	12.195	0.410	0.984	10.526	0.785	0.970
Pb^{2+}	10.52	0.257	0.978	6.94	0.304	0.984
Ni^{2+}	11.76	0.298	0.982	10	0.31	0.979

Table 4. Parameters of Freundlich isotherm for ion exchange of metal ions on zeolite and purolite C105.

Metal	Zeolite			Purolite C105		
	k_f	1/n	R^2	k_f	1/n	R^2
Cu^{2+}	6.745	0.127	0.811	6.194	0.119	0.593
Pb^{2+}	5.321	0.139	0.716	4.764	0.123	0.554
Ni^{2+}	6.266	0.129	0.700	5.147	0.116	0.638

Table 5. Parameters of BET isotherm for ion exchange of metal ions on zeolite and purolite.

Metal	Zeolite			Purolite C105		
	a	b	R^2	a	b	R^2
Cu^{2+}	76.923	13	0.584	28.571	1.522	0.60
Pb^{2+}	3.115	1.122	0.527	6.097	1.123	0.14
Ni^{2+}	27.778	1.636	0.690	7.875	1.165	0.68

Table 6. Adsorption rate constants, estimated qe and coefficients of correlation associated to the Lagergren first order model for zeolite resin.

metal	$q_{e,exp}$ (mg g^{-1})	$K_1 \times 10^3$ (min^{-1})	q_e (mg g^{-1})	R^2
Cu^{2+}	9.74	11	8.414	0.985
Pb^{2+}	9.23	12	9.715	0.999
Ni^{2+}	9.71	11	9.247	0.989

Table 7. Lagergren first order model for purolite C105 resin.

metal	$q_{e,exp}$ (mg g^{-1})	$K_1 \times 10^3$ (min^{-1})	q_e (mg g^{-1})	R^2
Cu^{2+}	9.64	11	9.016	0.985
Pb^{2+}	8.73	10	9.099	0.979
Ni^{2+}	9.39	8	9.12	0.995

Table 8. adsorption rate constants, estimated q_e and coefficients of correlation associated to the Lagergren second order model for zeolite resin.

metal	$q_{e,exp}$ (mg g^{-1})	$K_2 \times 10^{-3}$ (g/mg.min)	q_e (mg g^{-1})	h	R^2
Cu^{2+}	9.74	3.689	12.82	0.35	0.99
Pb^{2+}	9.23	2.348	15.873	0.2	0.93
Ni^{2+}	9.71	2.864	14.084	0.27	0.97

Table 9. adsorption rate constants, estimated qe and coefficients of correlation associated to the Lagergren second order model for purolite C105 resin.

metal	$q_{e,exp}$ (mg g^{-1})	$K_2 \times 10^{-3}$ (g/mg.min)	q_e (mg g^{-1})	h	R^2
Cu^{2+}	9.64	3.659	12.5	0.34	0.99
Pb^{2+}	8.73	2.493	14.08	0.19	0.93
Ni^{2+}	9.39	3.17	12.66	0.28	0.98

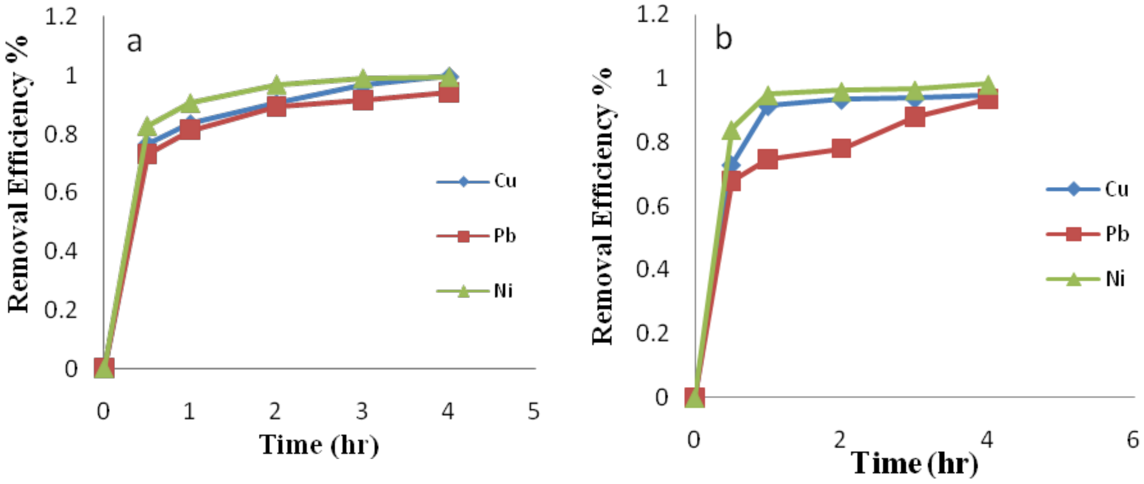

Fig. 1. Effect of contact time on removal of heavy metals on (a)zeolite,(b) purolite C105. (pH 6; m=0.5 g; 200 rpm; C_o=100 mg/L).

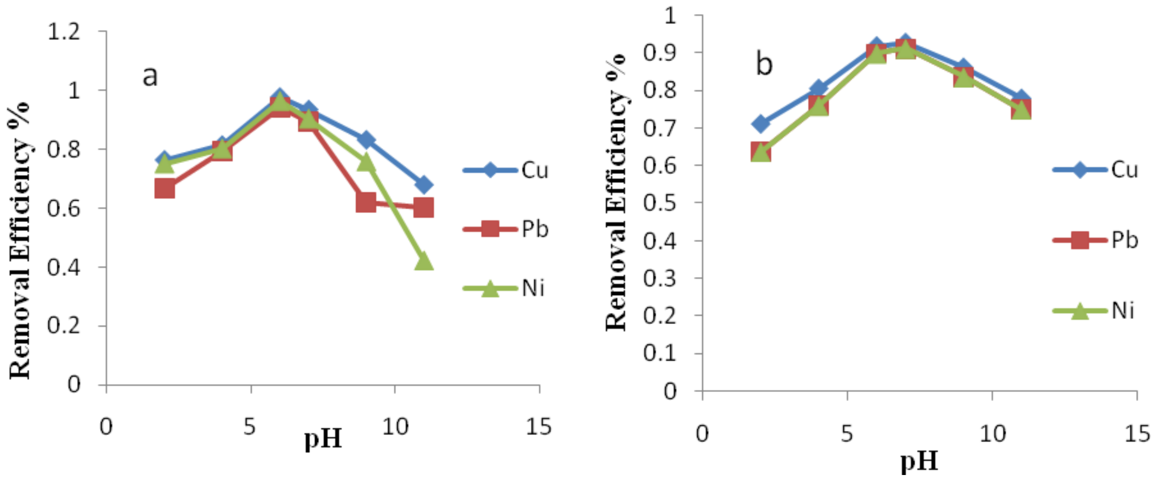

Fig. 2. Effect of pH on removal of heavy metals on (a) zeolite (b) purolite C105. (2hrs, m=0.5 g; 200 rpm; C_o= 100 mg/L).

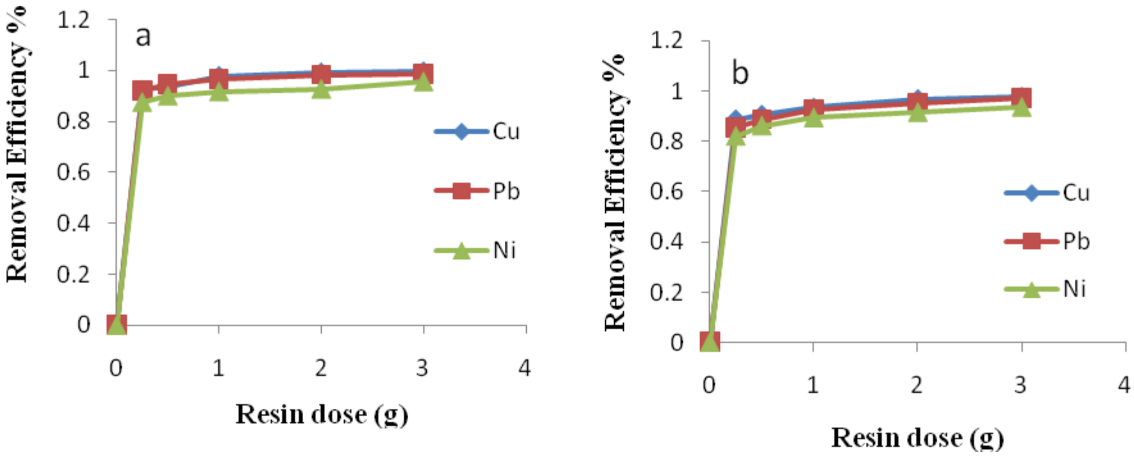

Fig. 3. Effect of resin dose on removal of heavy metals on (a) zeolite, (b) purolite C105. (2 hrs, pH 6, 200 rpm, C_0=100 mg/L).

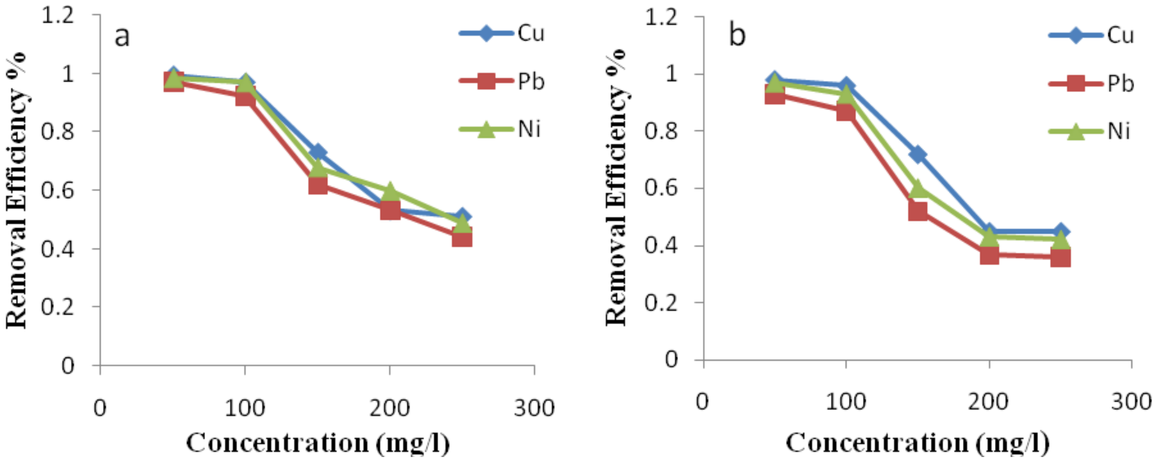

Fig. 4. Effect of initial concentration on removal of heavy metals on(a)zeolite,(b)purolite C105 resin (pH 6, m=0.5 g, 200 rpm, 2 hrs).

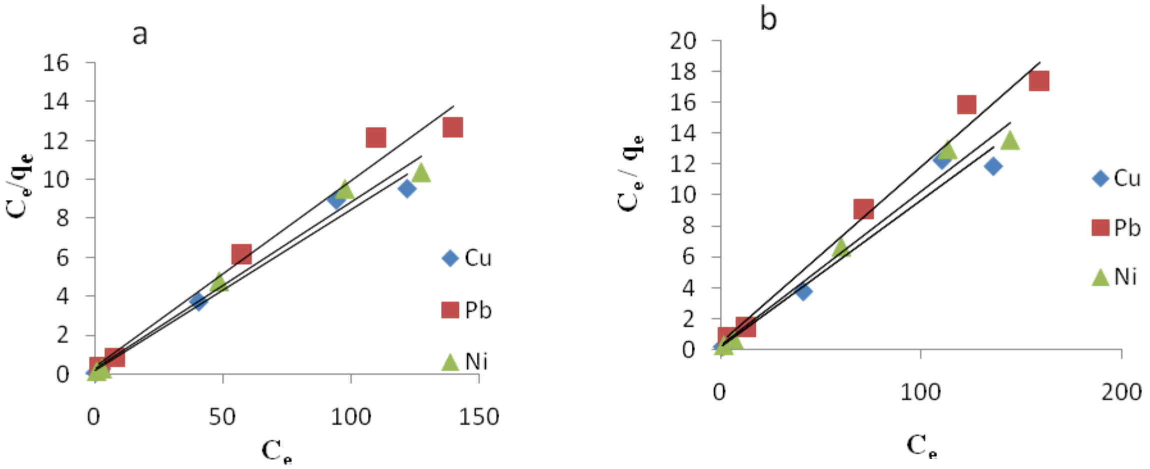

Fig. 5. Langmuir isotherm for ion exchange of copper, lead, and Nickel on (a) zeolite,(b) puroliteC105 (pH 6; 200rpm; m= 0.5g).

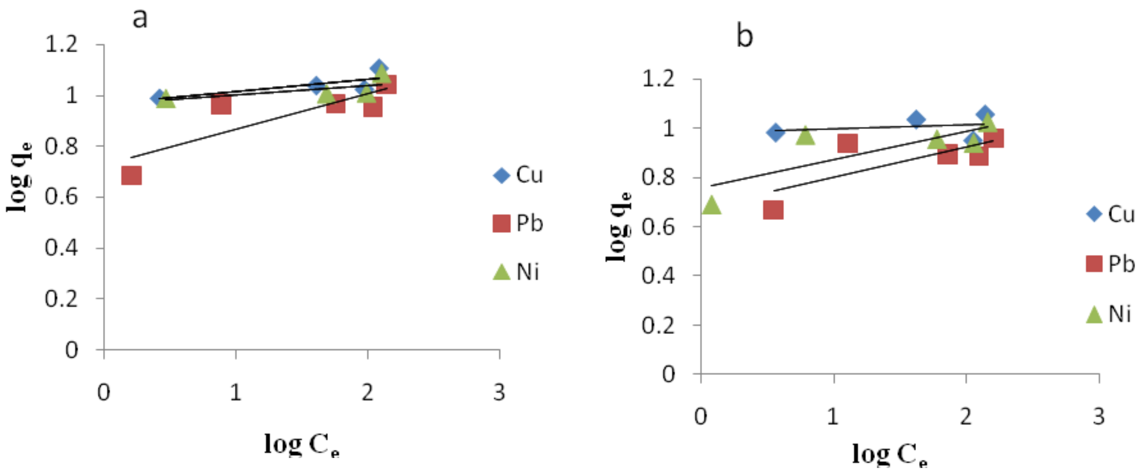

Fig. 6. Freundlich isotherm for ion exchange of copper, lead and Nickel on(a) zeolite,(b) purolite C105 (pH 6; 200 rpm; m= 0.5g).

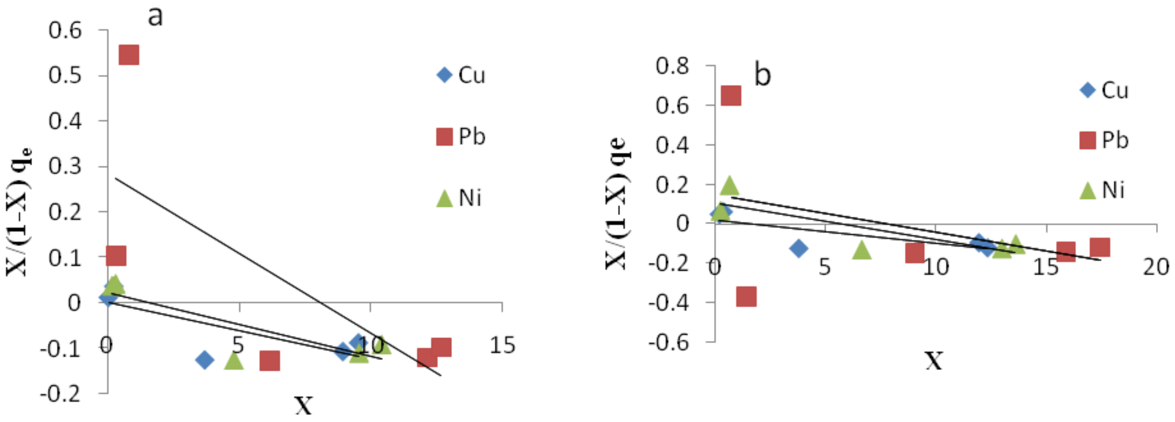

Fig. (7): BET isotherm for ion exchange of copper, lead, and Nickel on (a) zeolite,(b) purolite C105 (pH7, 200rpm; m=0.5g).