International Journal of Water Resources and Environmental Engineering Vol. 4(6), pp. 192-200, June 2012
Available online at http://www.academicjournals.org/IJWREE
DOI: 10.5897/IJWREE11.088
ISSN 1991-637X ©2012 Academic Journals

Full Length Research Paper

Kinetic studies on the removal of some metal ions from aqueous solution using modified orange mesocarp extract

Millicent U. Ibezim-Ezeani*, Francis A. Okoye and Onyewuchi Akaranta

Department of Pure and Industrial Chemistry, University of Port Harcourt, Choba, Port Harcourt, Rivers State, Nigeria.

Accepted 6 April, 2012

This study examines the kinetics of the removal of zinc, copper, nickel and cobalt ions from aqueous solutions by Carboxylated-Toluene Di-isocyanate Orange Mesocarp Extract Resin (CTOR) and Sulphonated-Toluene Di-isocyanate Orange Mesocarp Extract Resin (STOR). Results from contact time experiments indicate that the rate of ion exchange was initially rapid and equilibrium was attained within 40 to 45 min. It was found that the uptake of Zn^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+} ions by CTOR and STOR is related to the dissociation power of the exchangeable hydrogen and in sequence similar to the ionic radii of the metal ions. The Vermeulen's particle diffusion model best described the ion exchange process. The fraction attainment of equilibrium (α) values increase with time and reaching constant value at about 40 to 45 min for the resins, indicating the time for saturation of the active sites. The rate constants for CTOR and STOR decreased with increase in temperature from 29 to 70°C. The negative values of the activation energy calculated using the Arrhenius equation showed that low temperatures favoured the exchange process.

Key words: Kinetics, orange mesocarp, ion exchange, metal ions, resin, diffusion.

INTRODUCTION

The amount of treated and untreated wastes discharged into water through domestic and industrial activities have deteriorated the water bodies and made them unfit for many of their purposes (ASTM, 1989). Physico-chemical treatment technique such as ion exchange has been reported to be effective in the removal of cations and anions from solutions (Englert and Rubio, 2005; Jorgensen and Weatherley, 2003). Ion exchange is a stoichiometric chemical reaction in which the interchange of equivalent ions at the phase boundary is reversible. An ion exchange resin therefore, is a solid consisting of a matrix of insoluble material interspersed with fixed ions of opposite charge and having the property of exchanging equivalent ions from solutions for useful applications (Nostrand, 1964). In this study, the kinetics of the interchange of mobile hydrated H^+ ions of synthesized orange mesocarp extract resin (solid phase) for equivalent ions of like charge (Zn^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+}) in aqueous phase was investigated. The rate of variation of concentration of the interchangeable and interchanging ionic species with time at a given temperature as the ion exchange process proceeds from non-equilibrium to an equilibrium state describes its kinetics.

The kinetics of exchange enables us to understand the viability of an ion exchange material in separation technology (Jignasa et al., 2006), helps in identifying the reaction pathway and rate dependence on the limiting reacting systems (Halligudi and Khaire, 2001). These rates and mechanisms are governed by ion exchange conditions, nature of the exchanger and the exchanging ionic species. Ion exchange is a diffusion phenomenom and the reaction (Rao et al., 2010) can be represented as:

$$2RH_{(s)} + M^{2+}_{(aq)} \leftrightarrow R_2M_{(s)} + 2H^+_{(aq)}$$

*Corresponding author. E-mail: millibejmj@yahoo.com. Tel: +2347039450740.

where R is the ion exchange radical, H is the exchangeable hydrogen, M^{2+} refers to exchanging metal ion , H^+ is the exchanged hydrogen ion, RH is the resin before exchange and R_2M is the resin after exchange.

Ion exchange kinetics involves the diffusion of M^{2+} through the solution to the surface and particle pores of the resin, followed by the chemical exchange between H^+ and M^{2+} at the exchanging sites and the diffusion of the displaced H^+ ions out of the interior and surface of the resin into the solution. Both film and particle diffusion mechanisms are prevalent in ion exchange process, although normally the slowest step (rate-limiting step) for a given system controls the speed of ion exchange (Sprynskyy et al., 2005; Elshazly and Konsowa, 2003; Cooney et al., 1999). Earlier studies noted that film diffusion control prevail in systems with ion exchangers of high concentrations of fixed ionic groups, small particle size, dilute solutions and with inefficient agitation (Sprynskyy et al., 2005), while high metal ion concentration, relatively large particle size of the exchanger and vigorous shaking of the exchanging mixture favour a particle diffusion controlled process (Jignasa et al., 2006; Helfferich, 1962). Therefore, the particle size of the resin affects the film and particle diffusion processes, thus determining the equilibration time and rate. Ogali et al. (2008) reported the use of unmodified orange mesocarp residue after extraction of rutin to bind 56% of Mg, 81% of Zn, 71% of Cu, 73% of Pb and 85.05% of Cd, while the modified residue using 2,4-Dichloro-6-(Phenoxy-4′-sulphonic acid)-1,3,5-triazine bound 63.05% of Mg, 37% of Zn, 43.25% of Cu, 33.05% of Pb and 86.45% of Cd. Previous investigation on the removal of zinc, copper, nickel and cobalt ions from aqueous solutions using orange mesocarp extract (OME) revealed low ion exchange capacities of 0.0073 mg/g for Zn^{2+}, 0.01 mg/g for Cu^{2+}, 0.01535 mg/g for Ni^{2+} and 0.0194 mg/g for Co^{2+} ions with 10 mg/L metal ion concentration, indicating the lesser ease of bond breaking between the exchangeable proton and the structure of the species, which in turn influences its displacement by metal ion. This suggested that the attachment of more electron withdrawing atoms to the active site-carbons of the OME will enhance proton dissociation.

Further experiments with OME, CTOR and STOR under the same reaction condition, showed their ion exchange capacities to be in the order: STOR > CTOR > OME. This trend is associated with the dissociation power of the hydrogen in the main ionogenic functional group of the exchanger in aqueous solution which is –OH for OME, $-CO_2H$ for CTOR and $–SO_3H$ for STOR (Ibezim-Ezeani et al., 2010). Also, the Dubinin-Radushkevich isotherm parameters revealed that the uptake of metal ion by OME proceeded by physical adsorption (Energy = 0.1581 kJ/mol), while the uptake of metal ion by CTOR and STOR proceeded by ion exchange mechanism (Energy = 8.452 – 11.180 kJ/mol).

The aim of this work is to determine the percentage ion exchange of the synthesized orange mesocarp extract resins at different particle sizes and agitation times, evaluate the rate controlling mechanism of the ion exchange process and as possible index in designing an effluent treatment plant of metal industries.

MATERIALS AND METHODS

Collection and preparation of orange mesocarp sample

Fresh oranges bought from Choba market in River State, Nigeria was utilized for this study. The oranges were washed with deionized water. The epicarp was peeled off, the mesocarp carefully removed from the succulent part and sun dried for eight days. The dried orange mesocarp was ground with a grinding mill, sieved with British Standard sieve plate to obtain 106 µm particle size and stored in a plastic container at ambient atmospheric condition.

Extraction of rutin

Rutin was extracted from 2810 g of 106 µm size orange mesocarp with soxhlet extractor using methanol as extracting solvent. The methanol was recovered from the extract mixture using rotor evaporator.

Synthesis of Carboxylated-toluene di-isocyanate orange mesocarp extract resin (CTOR)

In a 1L beaker containing 53 g of 4-Hydroxybenzoic acid dissolved in 140 ml of acetone, 80 g of extract in 120 ml of methanol was added and stirred vigorously for 10 min at room temperature (29°C). 200 ml of toluene diisocyanate (TDI) was poured into the mixture with continuous stirring; the resultant product was off-white coloured solid. The resin formed was left overnight before use. This was then crushed, sieved to different sizes and stored in tightly covered bottles at room temperature.

Synthesis of sulphonated-toluene di-isocyanate orange mesocarp extract resin (STOR)

In a 1L beaker containing 40 ml 4-Hydroxybenzene sulphonic acid in 90 ml of acetone, 80 g of extract in 120 ml of methanol was added and stirred vigorously for 10 min at room temperature (29°C). 200 ml of toluene diisocyanate (TDI) was poured into the mixture with continuous stirring; the resultant product was off-white colored solid. The resin formed was left overnight before use. This was then crushed, sieved to different sizes and stored in tightly covered bottles at room temperature.

Preparation of metal ion stock solutions

4.397 g of Zn^{2+} ($ZnSO_4.7H_2O$), 3.803 g of Cu^{2+} [$Cu(NO_3)_2.3H_2O$], 4.460 g of Ni^{2+} ($NiSO_4.6H_2O$) and 4.770 g of Co^{2+} ($CoSO_4.7H_2O$) were each dissolved in 1.0L of distilled deionised water to obtain 1000 mg/L metal ion stock solution respectively. Dilution of the stock solutions was carried out to obtain working standards of 50 mg/L solutions for Zn (II), Cu (II), Ni (II) and Co (II) ions.

Ion exchange studies

One gram of CTOR sample was added to 50 ml of 50 mg/L metal

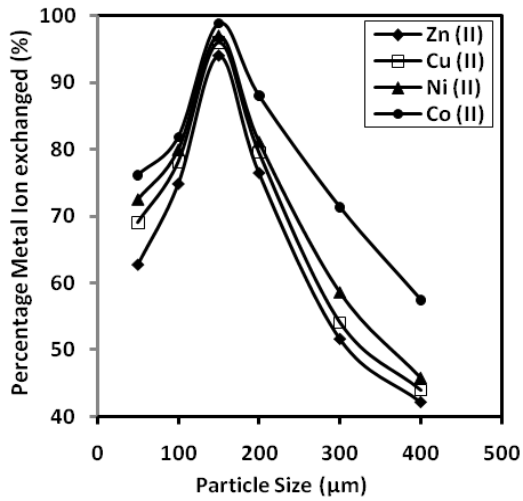

Figure 1. Plot of percentage metal ion exchanged as a function of resin particle size for CTOR.

Ion exchange studies

One gram of CTOR sample was added to 50 ml of 50 mg/L metal (Zn^{2+} / Cu^{2+} / Ni^{2+} / Co^{2+}) ion solution in 150 ml conical flask and corked. The flask was then shaken in a mechanical shaker (120 oscillations/min) for one hour at 29°C. After the shaking period, the solution was filtered through a glass wool and the concentration of metal ion (Zn^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+}) in the filtrate analysed using the Buck Scientific Atomic Absorption Spectrophotometer (model 205 A). The above experiment was repeated at various particle sizes (≈50 to ≈600 µm) and agitation times (1 to 60 min). The percentage metal ion exchange (%) was calculated using Equation (1) and plotted as a function of particle size and agitation time in each case. The experiments were repeated using STOR.

Kinetic measurements

One gram of CTOR sample was placed in several conical flasks containing 50 ml of 50 mg/L metal (Zn^{2+} / Cu^{2+} / Ni^{2+} / Co^{2+}) ion solution and corked. The flasks were shaken vigorously in a mechanical shaker (120 oscillations/min) at 29°C and the samples withdrawn at different time intervals. On withdrawal, the solution was filtered through a glass wool and the concentration of metal ion (Zn^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+}) in the filtrate analysed using the Buck Scientific Atomic Absorption Spectrophotometer (model 205 A) at Ideyi Consults Limited, Choba, Port-Harcourt. The above experiment was repeated at temperatures of 40, 50 and 60°C. The values obtained were used in the calculation of fractional attainment of equilibrium (Equation 2) (Sekar et al., 2004) for application in the Vermeulen particle and film diffusion equation (Equations 3 and 4 respectively) (Sprynskyy et al., 2005) plots, for the determination of the overall rate constant (Equation 5) (Jignasa et al., 2006; Karthikeyan et al., 2004; Loukidou et al., 2004) and activation energy (Equation 6) (Ibezim-Ezeani and Anusiem, 2010; Atkins, 1998). The experiments were repeated using STOR.

Data analysis

$$\% \text{ Metal Ion exchange} = \frac{C_o - C_e}{C_o} x\,100 \quad (1)$$

$$\frac{C_o - C_t}{C_o - C_e} = \alpha \quad (2)$$

where C_o is the initial concentration of metal ion in solution (mg/L), C_t is the concentration of metal ion in solution at any time, t (mg/L), C_e is the concentration of metal ion present at equilibrium (mg/L) and α is the fractional attainment of equilibrium of metal ion.

$$-\ln\left(1-\alpha^2\right) = t\left(\frac{D_p \pi^2}{r_p^2}\right) \quad (3)$$

$$-\ln\left(1-\alpha\right) = t\left(\frac{3D_f C_o}{r_p \delta C_e}\right) \quad (4)$$

where D_f is the diffusion coefficient in the film (m^2/s), C_o and C_e are concentrations in the solution and in the ion exchanger, respectively (mol/m^3), δ is the film thickness, D_p is the diffusion coefficient in the ion exchanger (m^2/s) and r_p is the radius of the particle (m).

The coefficient of determination (R^2) measurements was used to determine the best fitting Vermeulen's diffusion model (Chase and Brown, I992).

$$\ln\left(1-\alpha\right) = -kt \quad (5)$$

$$\ln k = \ln A - \frac{Ea}{RT} \quad (6)$$

where k is the rate constant, A is the pre-exponential factor, Ea is the activation energy, R is gas constant and T is temperature.

RESULTS AND DISCUSSION

Effect of particle size

The physical size of an ion exchanger influences its efficiency (Nada et al., 2002) and the time required to establish equilibrium conditions. Hence, the synthesized CTOR and STOR were ground and sieved to different particle sizes ranging from ≈50 to ≈600 µm and applied in the test for the effect of particle size on the ion exchange reaction (Figure 1 for CTOR and Figure 2 for STOR).

Figure 1 shows that there is an initial increase in the percentage metal ion exchange (from 62.74 to 94.02% for Zn^{2+}, 69.06 to 96.00% for Cu^{2+}, 72.56 to 97.08% for Ni^{2+} and 76.14 to 98.84% for Co^{2+}) with increase in particle size from ≈50 to ≈150 µm, followed by a decrease in percentage metal ion exchange with increase in particle size of CTOR, suggesting the ≈150 µm particle size as the suitable size for the ion exchange process. It could be that at lower particle size, the CTOR molecule experienced swelling and clogging together on immersion into aqueous solution, and as such inhibiting the diffusion of metal ions through it to the exchange sites. At ≈150 µm particle size, it may be that the resin particle presented

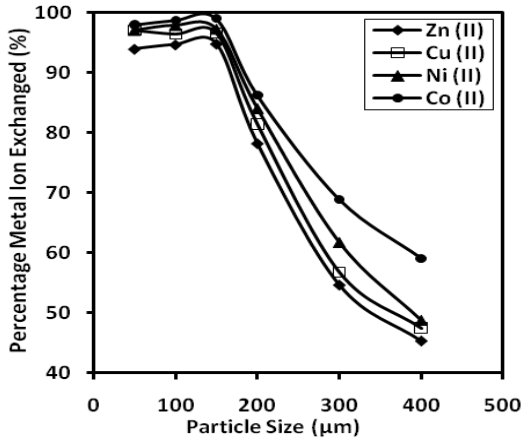

Figure 2. Plot of percentage metal ion exchanged as a function of resin particle size for STOR.

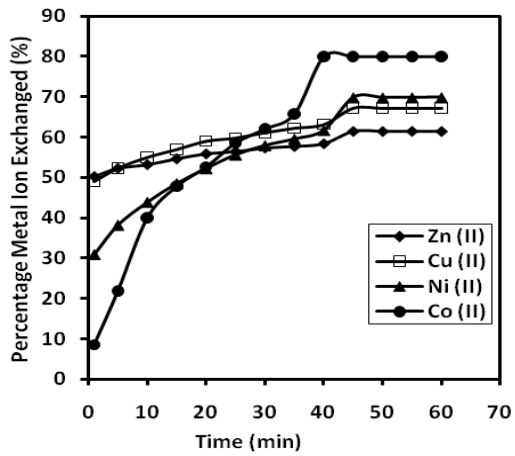

Figure 3. Plot of percentage metal ion exchanged at different agitation times for CTOR.

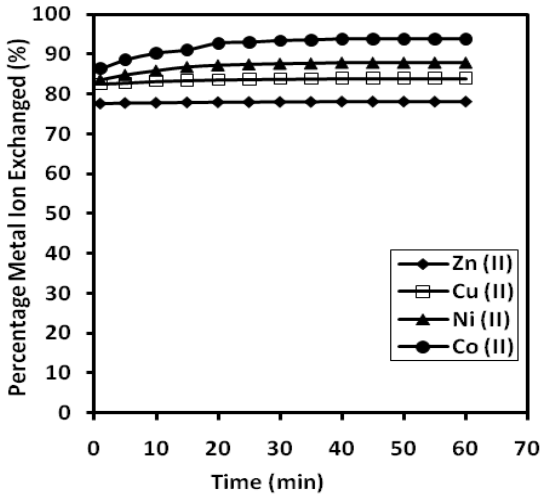

Figure 4. Plot of percentage metal ion exchanged at different agitation times for STOR.

better orientation for the diffusion of metal ions from surrounding solution to the surface of the CTOR particle, and also contains less internal volume (as compared to the particle sizes >150 µm) through which the metal ion diffuse from the surface to the interior of the resin particle, thus enhancing the efficiency of the 150 µm particle size exchanger.

In the case of STOR (Figure 2), the resin efficiency was fairly constant initially, but decreased (from 94.78 to 45.28% for Zn^{2+}, 96.54 to 47.46% for Cu^{2+}, 97.22 to 48.76% for Ni^{2+} and 98.96 to 59.04% for Co^{2+}) beyond the 150 µm particle size. This behaviour could be explained based on the smaller sizes and increased number of binding sites of the STOR particles between ≈50 and ≈150 µm, than that of larger dimensions beyond the 150 µm size. It is likely that with the smaller particle sizes, the percentage metal ion exchange is higher due to increase in its surface area and easier access of the metal ions to the better exposed active sites (Venkateswarlu et al., 2007), while in the case of larger particles, the diffusional resistance to mass transport is higher and most of the internal surface of the particles may not be utilized for ion exchange reaction (Sekar et al., 2004), consequently leading to smaller metal ion exchange.

In terms of the metal ion exchange, the percentage ion exchange is in the order: Co^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}. The order is similar to the order of the ionic radii (Zn^{2+} = 0.74 Å, Cu^{2+} = 0.73 Å, Ni^{2+} = 0.69 Å and Co^{2+} = 0.65 Å) of the metal ions (Lee, 1996), suggesting that the smaller the radius of the metal ion, the easier its diffusion to the exchange sites and hence, the higher the percentage ion exchange. In this case, Co^{2+} with the smallest radius and greatest access to the exchange sites, exhibited the highest percentage ion exchange followed by Ni^{2+}, Cu^{2+} and Zn^{2+} ions. This observation is in conformity with that of previous works (Erdem et al., 2004; Zoumpoulakis and Simitzis, 2001).

In view of the above discussion, the ≈150 µm particle sizes of CTOR and STOR were used for the remaining experiments.

Effect of agitation time

The effect of agitation on the ion exchange reaction at different times was investigated since earlier studies revealed that agitation facilitates proper contact between the metal ions in solution and the exchange sites, thereby promoting effective transfer of metal ions to the binding sites (Ahalya et al., 2005). The data from the time dependency experiment for the ion exchange of Zn^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+} ions are shown in Figure 3 for CTOR and Figure 4 for STOR.

For the CTOR experiments, result analysis showed that the percentage exchange of the metal ions increased from 50.24 to 61.48% for Zn^{2+}, 48.92 to 69.24% for Cu^{2+},

Table 1. Comparison of coefficients of determination (R^2) for the Vermeulen particle and film diffusion models.

Metal Ion	CTOR		STOR	
	Film diffusion -ln(1- α)	Particle diffusion -ln(1- α^2)	Film diffusion -ln(1- α)	Particle diffusion -ln(1- α^2)
Zn (II)	0.9951	0.9957	0.9944	0.9945
Cu (II)	0.9966	0.9972	0.9945	0.9946
Ni (II)	0.9981	0.9983	0.9755	0.9761
Co (II)	0.9904	0.9950	0.9867	0.9872

30.92 to 69.82% for Ni^{2+} and 8.54 to 79.96% for Co^{2+} ions within 40 to 45 min of the agitation time and thereafter remained relatively uniform. This observed initial increase in percentage exchange with agitation time could be due to the decrease in boundary layer resistance to mass transfer in the bulk and an increase in the kinetic energy of hydrated metal ions. Earlier study by Horsfall and Abia (2003) reported similar observations. The final stage of uniformity in the percentage ion exchange could be related to the attainment of equilibrium time which signifies the time required for the active sites on the exchanger to be saturated with the exchanged metal ions. Vinodhini et al. (2010), Arivoli and Thenkuzhali (2008) and Ho (2006) have all observed the same saturation as a function of time in their various studies.

For the STOR experiments, result of analysis showed that the percentage ion exchange increased slightly (from 77.60 to 78.10% for Zn^{2+}, 82.58 to 83.98% for Cu^{2+}, 84.72 to 88.00% for Ni^{2+} and 86.40 to 93.82% for Co^{2+}) with agitation time, and then reaching equilibrium time at about 30 to 35 min, suggesting that agitation time has very little effect on the percentage exchange of the metal ions with STOR. This is significant as equilibrium time is an essential parameter for economical water and wastewater applications.

Also, In terms of the metal ions tested, the percentage ion exchange is in the order: $Co^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$ which conforms with that of their ionic radii as earlier discussed. The results also confirm that the period of shaking (1 h) used was sufficient for the attainment of equilibrium.

Kinetics study

Kinetic data are essential for scaling up of ion exchange reactions for industrial preparation (Halligudi and Khaire, 2001). Hence, the time dependency experiments were carried out at various temperatures (29, 40, 50, 60 and 70°C) to ascertain the rates and mechanism involved in the exchange reaction. Data analyses showed that the fraction attainment of equilibrium (α) values increase with time and reaching a constant value at about 40 to 45 min for the resins, indicating the time for coverage of available binding sites. In all the experiments, the values of α for STOR were higher than those of CTOR. It is reasonable to infer that the greater ease of dissociation of STOR will influence its rate of dissociation with time (Ibezim-Ezeani et al., 2010), resulting in higher values of α for STOR both at the initial and equilibrium time.

In this investigation, the Vermeulen particle and film diffusion models (Equations 3 and 4) were used to fit the kinetic experimental data and the values of coefficient of determination, R^2 are presented in Table 1.

The values of coefficient of determination from the plots were close suggesting an interplay of film and particle diffusion in the exchange process. However, the best fits in the whole data range were found with the Vermeulen's particle diffusion model which exhibited higher values of coefficient of determination. This indicates that the rate – controlling mechanism for the exchange reaction is particle diffusion. In the study of ammonium removal from aqueous solution by natural zeolite and transcarpathian mordenite, Sprynskyy et al. (2005) remarked that the ion exchange with the homoionic mordenite forms exhibited the best correlation with diffusion model, while the coarser zeolite fraction demonstrates the poorest fit to the film, apparently due to the mineralogical separation or the structural features of the different fractions.

In order to predict the rate of the ion exchange reaction, the kinetic model in Equation 5 was applied to the kinetic measurements from various temperature experiments and presented in Figures 5 to 9 for CTOR (linear equations in Table 2) and Figures 10 to 14 for STOR (linear equations in Table 3).

The plots of ln (1 - α) versus time at different temperatures were linear confirming that the ion exchange process is particle diffusion controlled. The value of the overall rate constant, k was deduced from the slope of the plots. These values reflect the rate of arrival of the metal ions to the surface of the active sites and the proportion of the ions that underwent exchange with time. Within the temperature range of the experiment, the values of k were higher for the STOR than CTOR, signifying more ion exchange by the STOR per time, while in terms of metal ion concentration, it is in the order: $Co^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$, which can be ascribed to their ionic radii, thus, the smaller the ionic radius, the easier diffusion, faster arrival of ions to the active sites, more interaction and ion exchange with time.

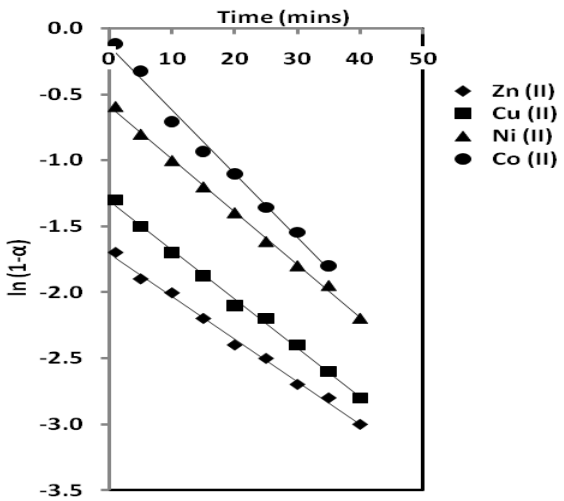

Figure 5. Plot of particle diffusivity against time for CTOR at 29°C.

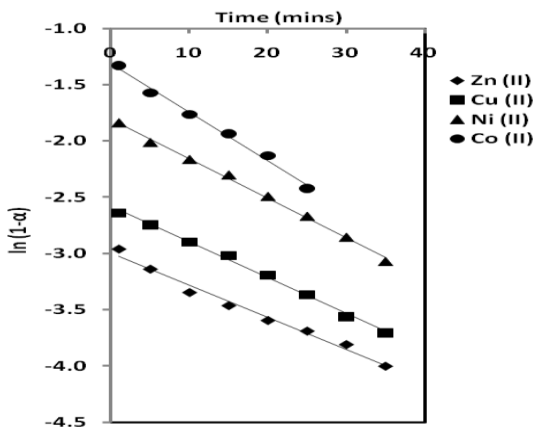

Figure 6. Plot of particle diffusivity against time for CTOR at 40°C.

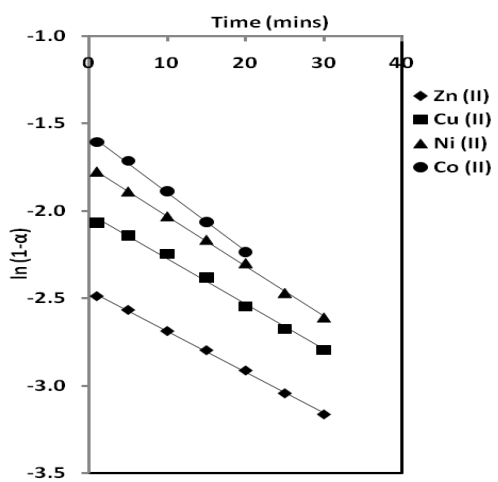

Figure 7. Plot of particle diffusivity against time for CTOR at 50°C.

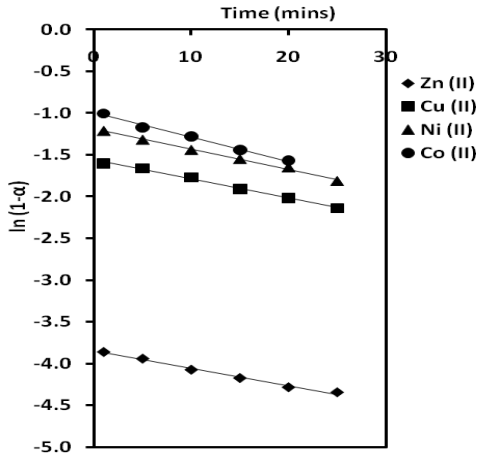

Figure 8. Plot of particle diffusivity against time for CTOR at 60°C.

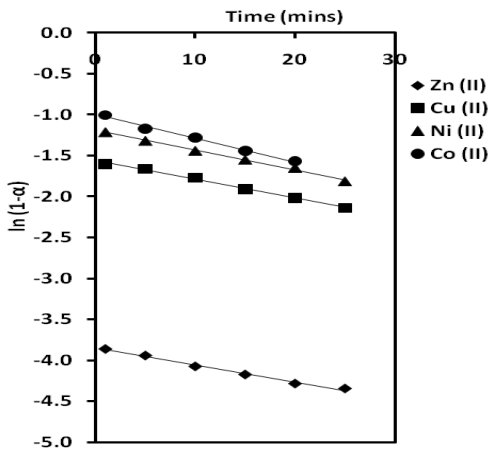

Figure 9. Plot of particle diffusivity against time for CTOR at 70°C.

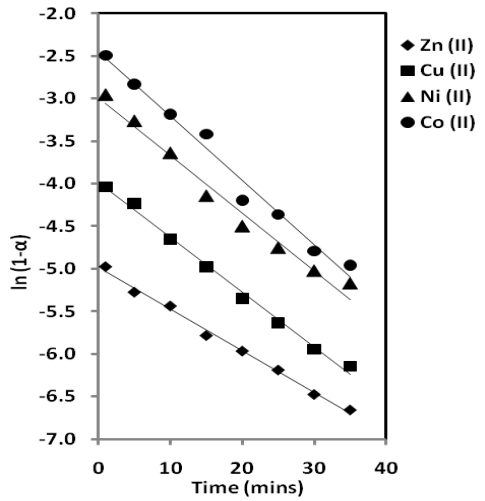

Figure 10. Plot of particle diffusivity against time for CTOR at 29°C.

Table 2. Linear equations from plots of particle diffusivity for CTOR.

Metal ion	29°C	40°C	50°C	60°C	70°C
Zn (II)	y = - 0.032x – 1.704	y = - 0.028x – 2.999	y = - 0.023x – 2.455	y = - 0.020x – 3.849	y = - 0.018x – 3.781
Cu (II)	y = - 0.037x – 1.304	y = - 0.031x – 2.581	y = - 0.026x – 2.014	y = - 0.022x – 1.561	y = - 0.020x – 2.423
Ni (II)	y = - 0.040x – 0.586	y = - 0.035x – 1.807	y = - 0.028x – 1.743	y = - 0.024x – 1.188	y = - 0.021x – 2.212
Co (II)	y = - 0.048x – 0.132	y = - 0.043x – 1.314	y = - 0.033x – 1.560	y = - 0.029x – 0.997	y = - 0.025x – 1.879

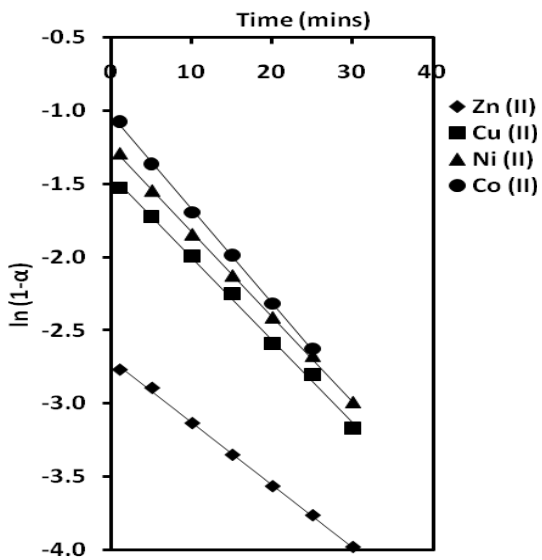

Figure 11. Plot of particle diffusivity against time for STOR at 40°C.

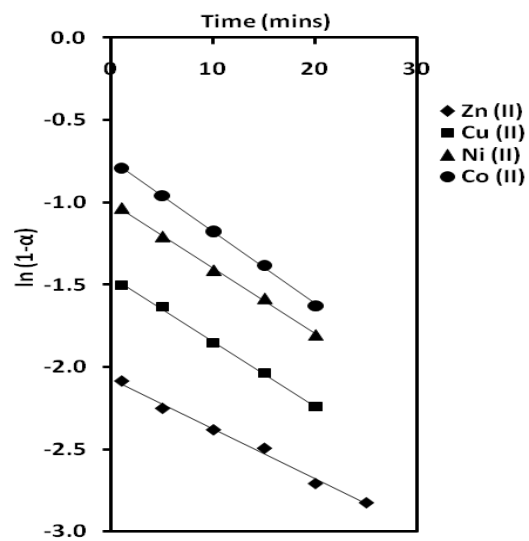

Figure 13. Plot of particle diffusivity against time for STOR at 60°C.

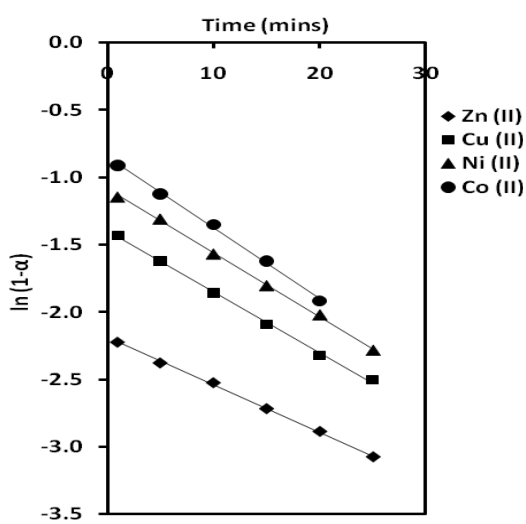

Figure 12. Plot of particle diffusivity against time for STOR at 50°C.

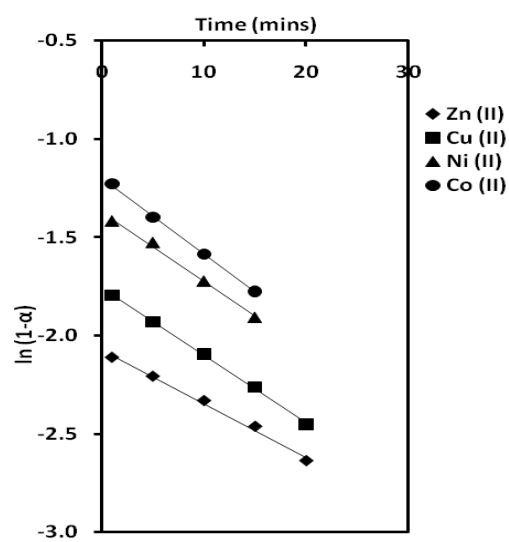

Figure 14. Plot of particle diffusivity against time for STOR at 70°C.

In all the experiments, k values decreased with increase in temperature, suggesting a distortion of the structural orientation of the STOR and CTOR, thereby altering the effective interaction of the metal ions with the exchanger, thus affecting the exchange rate. An identical trend was observed by other investigators in their various

Table 3. Linear equations from plots of particle diffusivity for STOR.

Metal ion	29°C	40°C	50°C	60°C	70°C
Zn (II)	y = - 0.049x – 4.982	y = - 0.042x – 2.707	y = - 0.035x – 2.189	y = - 0.030x – 2.074	y = - 0.027x – 2.072
Cu (II)	y = - 0.064x – 3.869	y = - 0.056x – 1.443	y = - 0.045x – 1.398	y = - 0.039x – 1.454	y = - 0.034x – 1.757
Ni (II)	y = - 0.067x – 2.986	y = - 0.057x – 1.248	y = - 0.047x – 1.087	y = - 0 039x – 1.001	y = - 0.035x – 1.370
Co (II)	y = - 0.076x – 2.441	y = - 0.064x – 1.031	y = - 0.052x – 0.852	y = - 0.043x – 0.742	y = - 0.038x – 1.196

Table 4. Activation energy values (Ea) for CTOR and STOR.

Metal ion	CTOR	STOR
	Activation energy (Ea) (kJ/mol)	Activation energy (Ea) (kJ/mol)
Zn (II)	-11.90	-12.57
Cu (II)	-12.80	-13.48
Ni (II)	-13.44	-13.92
Co (II)	-13.93	-14.32

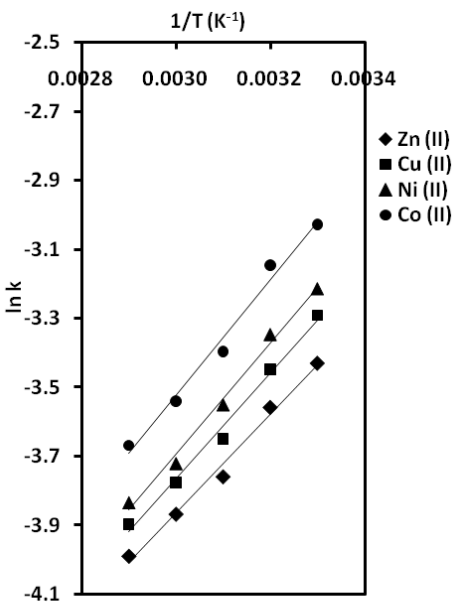

Figure 15. Plot of natural logarithm of rate constant at different temperatures for CTOR.

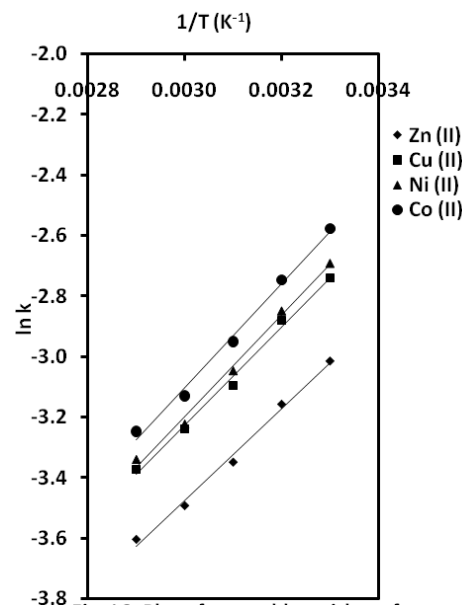

Figure 16. Plot of natural logarithm of rate constant at different temperatures for STOR.

researches (Ho and Chiang, 2001; Vinod and Anirudhan, 2001).

The validity of Arrhenius equation was verified by applying the values of k at temperatures of 29 to 70°C (Figure 15 for CTOR and Figure 16 for STOR) into Equation 6 and the values of Ea were then evaluated from the slope of the plots (Table 4).

The negative values of Ea indicate that the exchange process is exothermic and that lower solution temperature favours the exchange reaction. The values of Ea for STOR were lower than those of CTOR suggesting that more of the interacting species with STOR will possess the minimum energy required to overcome the energy barrier for ion exchange to occur. Also, for the metal ions, the negative values of Ea is in the order: $Co^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$, which is in line with that of their ionic radii indicating that the smaller the radius of the metal ion, the easier its access to the exchanger and the lesser the energy required to pass through the activated complex for the exchange reaction to take place.

Conclusion

The results obtained in this study suggest that the synthesized resins can be exploited as ion exchangers in the uptake of metal ions from aqueous solutions. Results from batch experiments showed that particle size and agitation time affect the ion exchange reaction.

Kinetically, the ion exchange process showed that particle diffusion was predominant, and that the process occurred at reasonable rate with low activation energy. Experimental results revealed that the ion exchange capacity is in the order: STOR > CTOR, which is of similar trend with their dissociation strength, while in terms of metal ion, the ion exchange capacity is in the order: Co^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}, which corresponds to the order of the ionic radii of the metal ions. The implementation of this finding will be useful in efficient orange mesocarp-waste management, enhance pollution free environment, prolong our life span and reduce the huge cost of purchasing commercial resins since orange mesocarp is a cheap and available agrowaste.

REFERENCES

Ahalya N, Kanamadi RD, Ramachandra TV (2005). Biosorption of Chromium (VI) from Aqueous Solutions by the Husk of Bengal Gram (*Cicer arientinum*). Elec. J. Biotechnol., 8(3): 1-8.

Arivoli S, Thenkuzhali M (2008). Kinetic, mechanistic, thermodynamic and equilibrium studies on the adsorption of rhodamine B by acid activated low cost carbon. Elec. J. Chem., 5(2): 187-200.

ASTM (1989). Annual Book of ASTM Standard. Water and Environment Technology, Philadelphia U.S.A., pp. 515-580.

Atkins PW (1998). Physical Chemistry, 6th ed. Oxford University Press, New York, pp. 775-777.

Chase W, Brown F (I992). General Statistics, 2nd ed. John Wiley and Sons, Inc. New York, pp. 610-630.

Cooney EL, Booker NA, Shallcross DC, Stevens GW (1999). Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-Scale study using continuous packed column process. Sep. Sci. Technol., 34(14): 2741-2760.

Elshazly AH, Konsowa AH (2003). Removal of nickel ions from wastewater using a cation-exchange resin in a batch-stirred tank reactor. Desalination, 158: 189-193.

Englert AH, Rubio J (2005). Characterization and environmental application of a chilean natural zeolite. Int. J. Miner. Process, 75: 21-29.

Erdem E, Karapinar N, Donat R (2004). The removal of heavy metal cations by natural zeolites. J. Coll. Interf. Sci., 280: 309-314.

Halligudi SB, Khaire SS (2001). Kinetics of hydrogen of 4-Chloro-2-Nitrophenol catalyzed by Pt/carbon catalyst. J. Chem. Technol. Biotechnol., 77: 25-28.

Helfferich F (1962). Ion Exchange, McGraw-Hill, New York, pp. 255-282.

Ho YS (2006). Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods. Water Res., 40: 119-125.

Ho YS, Chiang CC (2001). Sorption studies of acid dye by mixed sorbents. Adsorption, 7: 139-147.

Horsfall M Jr, Abia AA (2003). Sorption of cadmium (II) and zinc (II) ions from aqueous solutions by cassava waste biomass (*Manihot sculenta vanz*). Water Resour., 37: 4913-4923.

Ibezim-Ezeani MU, Anusiem ACI (2010). Kinetic studies of adsorption of palmitate and laurate soaps onto some metal ores in aqueous media. Int. J. Phys. Sci., 5: 62-67.

Ibezim-Ezeani MU, Okoye FA, Akaranta O (2010). Studies on the ion exchange properties of modified and unmodified orange mesocarp extract in aqueous solution. Int. Arch. Appl. Sci. Technol., 1: 33-40.

Jignasa A, Thakkar R, Uma C (2006). A study on equilibrium and kinetics of ion exchange of alkaline earth metals using an inorganic cation exchanger – zirconium titanium phosphate. J. Chem. Sci., 118(2): 185-189.

Jorgensen TC, Weatherley LR (2003). Ammonia removal from wastewaters by ion exchange in the presence of organic contaminants. Water Res., 37: 1723-1728.

Karthikeyan G, Anbalagan K, Andal NM (2004). Adsorption dynamic and equilibrium studies of Zn (II) onto chitosan. J. Chem. Sci., 116(2): 119-127.

Lee JD (1996). Concise Inorganic Chemistry, 5th edn., Blackwell Publishing Inc. U.S.A, pp. 786-839.

Loukidou MX, Thodoris DK, Zouboulis AI, Matis KA (2004). Diffusion kinetic study of chromium (VI) biosorption by *Aeromonas caviae*. Ind. Eng. Chem. Res., 43: 1748-1755.

Nada AMA, Eid MA, El RM, Khalifa MN (2002). Preparation and characterization of cation exchangers from agricultural residues. J. Appl. Polymer. Sci., 85: 792-800.

Nostrand DV (1964). International Encyclopedia of Chemical Science, D. Van Nostrand Company, Inc. New York, p. 620.

Ogali RE, Akaranta O, Aririguzo VO (2008). Removal of some metal ions from aqueous solution using orange mesocarp. Afr. J. Biotechnol., 7(17): 3073-3076.

Rao KS, Mohapatra M, Anand S, Venkateswarlu P (2010). Review on cadmium removal from aqueous solutions. Int. J. Eng. Sci. Technol., 2(7): 81-103.

Sekar M, Sakthi V, Rengaraji S (2004). Kinetics and equilibrium adsorption study of lead (II) onto activated carbon prepared from coconut shell. J. Coll. Interf. Sci., 279: 307-313.

Sprynskyy M, Lebedynets M, Zbytniewski R, Namieśnik J, Buszewski B (2005). Ammonium removal from aqueous solution by natural zeolite, transcarpathian mordenite, kinetics, equilibrium and column tests. Sep. Purif. Technol., 46: 155-160.

Venkateswarlu P, Ratnam MV, Rao DS, Rao MV (2007). Removal of chromium from an aqueous solution using *Azadirachta indica* (Neem) leaf powder as an adsorbent. Int. J. Phys. Sci., 2(8): 188-195.

Vinod VP, Anirudhan TS (2001). Sorption of tannic acid on zirconium pillared clay. J. Technol. Biotechnol., 77: 92-101.

Vinodhini V, Anabarasu V, Das N (2010). Screening of natural waste products for the removal of Cr (IV) ions from industrial effluents. Indian J. Nat. Prod. Resour., 1(2): 174-180.

Zoumpoulakis L, Simitzis J (2001). Ion exchange resins from phenol/formaldehyde resin-modified lignin. Polymer Int., 50: 277-283.