Equilibrium Studies of Some Metal Ions onto Modified Orange Mesocarp Extract in Aqueous Solution

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Authors' contributions

This work was carried out in collaboration between all authors. MUI-E designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. FAO and OA managed the analyses of the study. OA managed the literature searches. All authors read and approved the final manuscript.

ABSTRACT

This paper examines the equilibrium removal of Zinc, Copper, Nickel and Cobalt ions from aqueous solutions by cation exchange resins synthesized using orange mesocarp extract. The percentage metal ion exchange of Carboxylated-Toluene Di-isocyanate Orange Mesocarp Extract Resin (CTOR) increased with increase in pH of the solution phase, while that of Sulphonated-Toluene Di-isocyanate Orange Mesocarp Extract Resin (STOR) was relatively uniform with increase in solution pH. The results also showed maximum ion exchange of 61.48%, 67.24%, 69.82% and 78.96% for Zn²⁺, Cu²⁺, Ni²⁺ and Co²⁺ ions respectively for CTOR, while 78.10%, 83.98%, 88.00% and 93.80% for Zn²⁺, Cu²⁺, Ni²⁺ and Co²⁺ ions respectively for STOR using 50mg/L metal ion solution at 29°C. It was found that the uptake of Zn²⁺, Cu²⁺, Ni²⁺ and Co²⁺ 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. Thermodynamic parameters were evaluated and values obtained show that the ion exchange process was spontaneous, exothermic and of low entropy value, suggesting strong interaction between the metal ions and the exchange sites. These findings can serve as parameters for designing ion exchange treatment systems for heavy metal-contaminated wastewater.
Keywords: Equilibrium; orange mesocarp; ion exchange; metal ions; pH; resin.

1. INTRODUCTION

Industrialization around the globe is the main source of inflow of heavy metals, from untreated and inadequately treated industrial wastewaters, into water bodies (Olowu et al., 2010; Palanisamy and Kavitha, 2010). These metals have deleterious effects on man and his environment, when in excess of permissible limits; hence the disposal of wastewaters containing heavy metals is always a challenge to industrialists and environmentalists (Sekar et al., 2004). Recently, wastewater treatment techniques using agrowastes have been reported (Shanmugavalli et al., 2006; Agiri et al., 2007; Iyagba and Opete, 2009; Qaiser et al., 2007; Zvinowanda et al., 2009; Vinodhini et al., 2010) agrowastes are readily available, affordable and biodegradable. Ion exchange resins have been used for the removal of metal ions from aqueous solutions (Rengaraj et al., 2004; Naushad et al., 2009; Mojiri, 2011; Chudasama and Patel, 2011; Shaidan et al., 2012). Almost all the commercially available ion exchange resins are from synthetic phenols and usually expensive. The use of naturally occurring phenolic compounds, from agrowastes, as replacement for synthetic phenols in the synthesis of ion exchange resins will reduce the cost of such resins and any negative impact of such agrowastes to the environment. An earlier study on the ion exchange properties of modified and unmodified orange mesocarp extract in aqueous solution reported the ion exchange capacities to be in the order: Sulphonated-Toluene Di-isocyanate Orange Mesocarp Extract Resin (STOR) > Carboxylated-Toluene Di-isocyanate Orange Mesocarp Extract Resin (CTOR) > OME, unmodified orange mesocarp extract (Ibezim-Ezeani et al., 2010). This trend was attributed to the dissociation strength of the hydrogen in the main ionogenic functional groups of the exchanger in aqueous solution, which are: – OH for OME, – CO₂H for CTOR and – SO₃H for STOR. Furthermore, 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 to 11.180 kJ/mol). Equilibrium study of ion exchange process between synthesized orange mesocarp extract resins and some metal ions in aqueous solution was carried out to ascertain the influence of temperature and pH on the energy transformations associated with the ion exchange process as metal ions migrate to the exchange sites from the solution. Ion exchange equilibrium could be described as the state in which competing forces and moments between the concentration of the exchanging ions in the solution and that at the exchange sites for a given system are evenly matched, in order to achieve a condition of steadiness. An insight into the equilibrium properties of the ion exchange process is therefore, of great relevance in accessing the tendency of the system to attain a state of minimum energy and maximum disorder. This study investigates the effect of pH and temperature on the ion exchange properties of CTOR and STOR, and evaluates the equilibrium parameters of the ion exchange process. The result will serve as a basis for quantitative stoichiometric considerations, which are fundamental for mathematical modeling and scale-up.
2. MATERIALS AND METHODS

2.1 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 juicy 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 106µm particle size and stored in a plastic container at ambient atmospheric condition.

2.2 Extraction of Rutin

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

2.3 Synthesis of Carboxylated-toluene Di-isocyanate Orange Mesocarp Extract Resin (CTOR)

In a 1L beaker containing 53g of 4-Hydroxybenzoic acid dissolved in 140ml of acetone, 80g of extract in 120ml of methanol was added and stirred vigorously. 200ml 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 (29°C).

2.4 Synthesis of Sulphonated-toluene Di-isocyanate Orange Mesocarp Extract Resin (STOR)

In a 1L beaker containing 40ml 4-Hydroxybenzene sulphonic acid in 90ml of acetone, 80g of extract in 120ml of methanol was added and stirred vigorously. 200ml 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 (29°C).

2.5 Preparation of Metal Ion Stock Solutions

4.397g of Zn$^{2+}$ (ZnSO$_4$.7H$_2$O), 3.803g of Cu$^{2+}$ [Cu(NO$_3$)$_2$.3H$_2$O], 4.460g of Ni$^{2+}$ (NiSO$_4$.6H$_2$O) and 4.770g of Co$^{2+}$ (CoSO$_4$.7H$_2$O) were each dissolved in 1.0L of distilled deionised water to obtain 1000mg/L metal ion stock solution respectively. Dilution of the stock solutions was carried out to obtain working standard of 50mg/L solutions for Zn (II), Cu (II), Ni (II) and Co (II) ions, the pH of these solutions were measured.

2.6 Ion Exchange Studies

1.0 gram of CTOR sample was added to 50ml of 50mg/L metal (Zn$^{2+}$/Cu$^{2+}$/Ni$^{2+}$/Co$^{2+}$) ion solution in 150ml 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 pH values (1.93 to 11.18) and temperatures (29 to 80°C). The percentage metal ion exchange (%) was calculated using equation (1) and plotted as a function of pH and temperature in each case. The experiments were repeated using STOR.

2.7 Equilibrium Studies

1.0 gram of CTOR sample was added to 50ml of 50mg/L metal (Zn$^{2+}$/Cu$^{2+}$/Ni$^{2+}$/Co$^{2+}$) ion solution in 150ml 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 pH of the filtrate measured. The experiment was repeated at temperatures of 40°C, 50°C and 60°C. From the pH values obtained, the H$^+$ ion concentration (mg/L) in solution at equilibrium was evaluated and substituted in the equilibrium constant expression (equation 3) for the determination of equilibrium constant, K. The experiments were repeated using STOR.

2.8 Data Evaluation

\[
\% \text{ Metal Ion exchange} = \frac{C_o - C_e}{C_o} \times 100 
\]  

Where C_o is the initial concentration of metal ion in solution (mg/L) and C_e is the concentration of metal ion present at equilibrium (mg/L).

Following the stoichiometrical representation (Equation 2) of ion exchange reaction (Rao et al., 2010), the equilibrium constant, K of the process can be expressed as (Equation 3):

\[
2RH(s) + M^{2+}(aq) \leftrightarrow R_2M(s) + 2H^+(aq)
\]

\[
K = \frac{[M^{2+}]/2}{[H^+]^2}
\]

Where [H$^+$] is the concentration of hydrogen ion exchanged, [M$^{2+}$] is the initial concentration of metal ion in solution, RH is the resin before exchange and R$_2$M is the resin after exchange.

Thermodynamic parameters such as change in the enthalpy, $\Delta H^o$, Gibbs free energy, $\Delta G^o$ and entropy, $\Delta S^o$ can be calculated from the variation of equilibrium constant, K (mg/L) with change in temperature, T using Equations 4 and 5 (Arivoli et al., 2008; Arivoli and Thenkuzhal, 2008; Vasu, 2008):

\[
\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}
\]

\[
\Delta G^o = \Delta H^o - T\Delta S^o
\]

The plot of ln K against 1/T is linear and $\Delta H^o$, $\Delta S^o$ and $\Delta G^o$ can be computed from the slope and intercept of the plots.
3. RESULTS AND DISCUSSION

3.1 Effect of pH

The degree of exchange of ions depend on the solution pH which influences the surface charge of the exchanger, concentration of the metal ions on the functional groups of the exchanger, degree of ionization and speciation of metal ions.

The effect of pH (range from 1.93 to 11.18) on the metal ion exchange with CTOR and STOR are presented Fig. 1 and Fig. 2 respectively. The results from experiments with CTOR showed an increase in percentage metal ion exchange with increase in solution pH at the different pH values tested. It was observed that increase in the pH of the metal ion solution from ≈ 1.92 to ≈ 4.05 showed a gradual rise in the percentage metal ion exchange (from 16.84 to 38.14% for Zn$^{2+}$, 26.62 to 46.16% for Cu$^{2+}$, 35.58 to 50.22% to Ni$^{2+}$ and 40.20 to 52.84% for Co$^{2+}$), while from pH values of ≈ 4.05 to ≈ 7.05, a rapid increase in percentage metal ion exchange (from 38.14 to 84.62% for Zn$^{2+}$, 46.16 to 86.14% for Cu$^{2+}$, 50.22 to 88.00% for Ni$^{2+}$ and 52.84 to 92.42% for Co$^{2+}$) was observed which tends to level-off at higher solution pH. This suggests that the extent of hydrogen ion exchange would depend on the relative concentration of the exchangeable hydrogen and hydrogen ion concentration of the medium (Igwe et al., 2005). From the results, it is likely that at lower solution, protons occupy virtually all exchange sites and its surrounding medium thereby shielding and inhibiting the diffusion of the metal ions to the exchange sites which will lead to decreased metal ion exchange. As the solution is increased, the positive surface charge density reduces and the concentration of hydrogen ion on the exchanger sites decrease resulting in the reduction of electrostatic repulsion between the positively charged metal ions and the exchange site which then enhances more ion exchange. At higher pH, the exchange sites become more negatively charged due to the presence of hydroxide ions in solution, causing an increase in electrostatic interaction between the exchange sites and the metal ions which favours higher exchange of the metal ion in the form of M$^{2+}$ and MOH$^+$ species.
investigators also noted an increase in metal ion uptake with increase in solution pH in their various research (Kadirvelu and Namasivayam, 2003; Santhy and Selvapathy, 2004; Shin et al., 2007). Studies on the effect of pH (range from 4 to 10) on the adsorption capacities of sodium-palmitate and sodium-laureate soaps onto galena, hematite and cassiterite showed gradual increase in the adsorption capacity with increase in pH until a maximum is reached. Beyond this pH of maximum adsorption, the adsorption capacity decreased with increase in pH. Comparison of the pH of maximum adsorption with the zero-point of charge of the adsorbents revealed that the maximum adsorption capacities occurred in the region of the zero-point of charge of each adsorbent at 29°C (Ibezim-Ezeani and Anusiem, 2011a).

The ion exchange reaction between the exchangeable hydrogen ions at the CTOR (R'H) surface and the metal ions (M^{2+}) may be described by the following chemical equations:

\[ 2R'H + M^{2+} + H^+ \leftrightarrow R'O_2M + 3H^+ \]  
\[ 2R'H + M^{2+} \leftrightarrow R'O_2M + 2H^+ \]  
\[ 2R'H + M^{2+} + OH^- \leftrightarrow R'O_2M + H_3O^+ \]  
\[ R'H + M^{2+} + OH^- \leftrightarrow R'MOH + H^+ \]

The results from experiments performed with STOR showed a high percentage of metal ion exchange and a very little increase in percentage metal ion exchange (from 84.92 to 93.34% for Zn^{2+}, 86.02 to 95.10% for Cu^{2+}, 87.28 to 96.40% for Ni^{2+} and 90.26 to 97.08% for Co^{2+}) with increase in solution pH in the pH range tested. A comparison of the increase in percentage ion exchange with increase in solution pH in the case of CTOR and the fairly uniform relationship in that of STOR, indicated that the exchange of metal ion is controlled by the extent of functional group dissociation in these exchangers. According to the literature, the acidity constant (pKa) of carboxylic groups, weak acidic sites, is between 3.5 and 5.5 (Fourest and Volesky, 1996; Yun et al., 2001), while the pKa of sulphonic acid, a strong acidic site, is around 1.5 (Crist et al., 1992). Evaluation of the acid dissociation constant (ka) from the pKa values gave between 3.16x10^{-4} and 3.16 x 10^{-6} for CTOR and about 3.16x10^{-2} for STOR. The higher ka of SO_3H group indicated that a large concentration of the sulphonic group on the STOR molecule will dissociate ions in the entire pH range tested, while the smaller value of ka for CO_2H suggests that a small concentration of the carboxylic group on the CTOR molecule will dissociate ions. Again, this explains the characteristic variation in the percentage metal ion exchange with CTOR at different conditions of the solution pH, implying that the ion exchange in the CTOR system is driven into completion with increasing OH^- ions (Baes et al., 1996). In the case of STOR, the fairly uniform trend recorded in ion exchange with increase in solution pH could be attributable to the role played by the SO_3H group on the exchanger. Hence, the selectivity for divalent cation over the H^+ ion in the acidic pH region might explained by simple electrostatic attraction which presumes that divalent cations are more attracted to negatively charged ionogenic groups than monovalent cations (Shin et al., 2007), while the preference for the divalent cations over the OH^- ion in the alkaline pH range could be discussed based on the repulsion of like charges between the OH^- ions in solution and the -SO_3H groups on the STOR.

The reaction equation for the ion exchange process with STOR (R"H) may be written as:

\[ 2R"H + M^{2+} \leftrightarrow R"O_2M + 2H^+ \]
3.2 Effect of Temperature

The effect of temperature on the exchange reaction was studied over the range of 29 to 80°C (Fig. 3 for CTOR and Fig. 4 for STOR).

Careful examination of the plots revealed that the magnitude of metal ion exchange decreased with increase in temperature from temperature 29 to 80°C. This suggests weak interaction between the active exchanger sites and the metal ions. Probably as temperature is increased, the exchanger (STOR/CTOR) experienced some form of deformation of its pore size due to increase in the temperature of the active surface centres, thus leading to distortion of the structural arrangement of the resin matrix and its proper orientation for effective interaction. It could also be that with increase in temperature, the attractive forces between the exchanger surface and the metal ions are weakened, thus leading to the decrease in the thickness of the boundary layer due to the increased tendency of the metal ion to escape from the surface of the exchanger to the solution phase. These discussed effects will certainly influence the ion exchange capacity of CTOR and STOR, thereby giving rise to decreased ion exchange with increase in temperature. This is consistent with what is expected in an exothermic process. Similar finding was reported by Ho and Chang (2001) in the sorption studies of acid dye by mixed sorbents. However, Sekar et al. (2004) in the kinetics and equilibrium adsorption study of lead (II) onto activated carbon prepared from coconut shell noted that an increase of temperature from 35 to 45°C increased the sorption of Pb (II) from 78.15 to 91.00%, indicating the process to be endothermic. The increase in uptake of Pb (II) with temperature may be due to the desolvation of the adsorbing species, the changes in the size of pores and the enhanced rate of intraparticle diffusion of adsorbate.

Moreover, in the whole temperature range tested, it was observed that the percentage metal ion exchange was higher for STOR than CTOR, apparently due to their dissociation strength as earlier stated (Ibezim-Ezeani et al., 2010), while the percentage metal ion exchange is in
the order: Co\(^{2+}\) > Ni\(^{2+}\) > Cu\(^{2+}\) > Zn\(^{2+}\) for the metal ions. This order could be explained based on their ionic radii difference (Zn\(^{2+}\) = 0.74Å, Cu\(^{2+}\) = 0.73Å, Ni\(^{2+}\) = 0.69Å and Co\(^{2+}\) = 0.65Å) (Lee, 1996) as previously discussed.

3.3 Equilibrium Study of Exchange Reaction

The equilibrium constant has been determined at temperatures between 29 and 60°C based on the law of mass action and the values presented in Tables 1 to 4 for CTOR and Tables 5 to 8 for STOR (where T is temperature, [M\(^{2+}\)] is Initial metal ion concentration, (pH\(_A\)) is solution pH before exchange reaction, [H\(^+\)]\(_A\) is hydrogen ion concentration before exchange reaction, (pH\(_B\)) is solution pH after exchange reaction, [H\(^+\)]\(_B\) is hydrogen ion concentration after exchange reaction, \([\{H^+\}_B - [H^+]_A]\) = [H\(^+\)] is concentration of hydrogen ion exchanged and K is equilibrium constant).

There is in general a decrease in equilibrium constant with increase in temperature for the metal ions and the resins. The decrease in equilibrium constant with increase in temperature may arise from the weakening of attractive forces between the metal ions and the exchanger, suggesting favourable exchange reaction at lower temperature and reduction in the intensity of exchange at higher temperature.

Thermodynamic parameters were deduced from the variation of the equilibrium constant with change in temperature (equations 4 and 5). The plot of ln K versus 1/T is linear (Fig. 5 for CTOR and Fig. 6 for STOR). The values of the slope and intercept of the linear plots were used in computing \(\Delta G^°\), \(\Delta H^°\) and \(\Delta S^°\) (Table 9).

The negative values of \(\Delta G^°\) indicate that the process is feasible and to a large extent spontaneous. The negative values of \(\Delta H^°\) confirmed the exothermic character of the reaction and that lower temperature favours the reaction. Studies on the removal of copper from wastewater by Gaikwad (2011) reported positive value of \(\Delta H^°\) (4.408 kJ/mol) indicating the endothermic nature of adsorption and suggests weak binding of the adsorbate species with active surface sites of adsorbent. Thermodynamic data analysis on the adsorption of palmitate and laurate soaps onto some metal ore surfaces revealed that the adsorption process is spontaneous, exothermic, physical in nature and related to the specific surface area of the adsorbents (Ibezim-Ezeani and Anusiem, 2011b). The negative values of \(\Delta S^°\) signify that the freedom of the metal ions is more restricted in the resin particles than in solution. Generally, it is observed that the negative values of \(\Delta G^°\), \(\Delta H^°\) and \(\Delta S^°\) are higher for the STOR than the CTOR, probably due to the higher dissociation strength of STOR as earlier discussed. In terms of the metal ions, the negative values of \(\Delta G^°\), \(\Delta H^°\) and \(\Delta S^°\) are in the order: Co\(^{2+}\) > Ni\(^{2+}\) > Cu\(^{2+}\) > Zn\(^{2+}\), which is in line with the trend of their ionic radii. This could indicate that the smaller the size of the metal ion, the greater its access to the exchange site for interaction and the greatly reduced its freedom at the exchanger – solution interface.
Table 1. Equilibrium constant (K) for the zinc ion exchange with CTOR

| T (°C) | 1/T(K⁻¹) | M²⁺(mg/L) | (pH)ₐ | [H⁺]ₐ(mol/L) | (pH)ₜ | [H⁺]ₜ(mol/L) | [H⁺]ₜ(mol/L) | [H⁺](mg/L) | K(mg/L) |
|--------|-----------|-----------|-------|--------------|-------|--------------|--------------|-------------|---------|
| 29     | 0.0033    | 50        | 6.31  | 4.898 x 10⁻⁷ | 1.52  | 0.0302       | 0.0302       | 30.1995     | 18.2402  |
| 40     | 0.0032    | 50        | 6.31  | 4.898 x 10⁻⁷ | 1.57  | 0.0269       | 0.0269       | 26.9153     | 14.4887  |
| 50     | 0.0031    | 50        | 6.31  | 4.898 x 10⁻⁷ | 1.60  | 0.0251       | 0.0251       | 25.1189     | 12.6191  |
| 60     | 0.0030    | 50        | 6.31  | 4.898 x 10⁻⁷ | 1.67  | 0.0214       | 0.0214       | 21.3796     | 9.1418   |

Table 2. Equilibrium constant (K) for the copper ion exchange with CTOR

| T (°C) | 1/T(K⁻¹) | M²⁺(mg/L) | (pH)ₐ | [H⁺]ₐ(mol/L) | (pH)ₜ | [H⁺]ₜ(mol/L) | [H⁺]ₜ(mol/L) | [H⁺](mg/L) | K(mg/L) |
|--------|-----------|-----------|-------|--------------|-------|--------------|--------------|-------------|---------|
| 29     | 0.0033    | 50        | 6.48  | 3.311 x 10⁻⁷ | 1.48  | 0.0331       | 0.0331       | 33.1131     | 21.9296  |
| 40     | 0.0032    | 50        | 6.48  | 3.311 x 10⁻⁷ | 1.55  | 0.0282       | 0.0282       | 28.1838     | 15.8866  |
| 50     | 0.0031    | 50        | 6.48  | 3.311 x 10⁻⁷ | 1.57  | 0.0269       | 0.0269       | 26.9153     | 14.4887  |
| 60     | 0.0030    | 50        | 6.48  | 3.311 x 10⁻⁷ | 1.65  | 0.0224       | 0.0224       | 22.3872     | 10.0237  |

Table 3. Equilibrium constant (K) for the nickel ion exchange with CTOR

| T (°C) | 1/T(K⁻¹) | M²⁺(mg/L) | (pH)ₐ | [H⁺]ₐ(mol/L) | (pH)ₜ | [H⁺]ₜ(mol/L) | [H⁺]ₜ(mol/L) | [H⁺](mg/L) | K(mg/L) |
|--------|-----------|-----------|-------|--------------|-------|--------------|--------------|-------------|---------|
| 29     | 0.0033    | 50        | 6.60  | 2.512 x 10⁻⁷ | 1.46  | 0.0347       | 0.0347       | 34.6737     | 24.0453  |
| 40     | 0.0032    | 50        | 6.60  | 2.512 x 10⁻⁷ | 1.51  | 0.0309       | 0.0309       | 30.9030     | 19.0999  |
| 50     | 0.0031    | 50        | 6.60  | 2.512 x 10⁻⁷ | 1.55  | 0.0282       | 0.0282       | 28.1838     | 15.8866  |
| 60     | 0.0030    | 50        | 6.60  | 2.512 x 10⁻⁷ | 1.63  | 0.0234       | 0.0234       | 23.4423     | 10.9908  |

Table 4. Equilibrium constant (K) for the cobalt ion exchange with CTOR

| T (°C) | 1/T(K⁻¹) | M²⁺(mg/L) | (pH)ₐ | [H⁺]ₐ(mol/L) | (pH)ₜ | [H⁺]ₜ(mol/L) | [H⁺]ₜ(mol/L) | [H⁺](mg/L) | K(mg/L) |
|--------|-----------|-----------|-------|--------------|-------|--------------|--------------|-------------|---------|
| 29     | 0.0033    | 50        | 6.71  | 1.950 x 10⁻⁷ | 1.42  | 0.0380       | 0.0380       | 38.0189     | 28.9088  |
| 40     | 0.0032    | 50        | 6.71  | 1.950 x 10⁻⁷ | 1.48  | 0.0331       | 0.0331       | 33.1131     | 21.9296  |
| 50     | 0.0031    | 50        | 6.71  | 1.950 x 10⁻⁷ | 1.53  | 0.0295       | 0.0295       | 29.5121     | 17.4193  |
| 60     | 0.0030    | 50        | 6.71  | 1.950 x 10⁻⁷ | 1.6   | 0.0251       | 0.0251       | 25.1189     | 12.6191  |
Table 5. Equilibrium constant (K) for the zinc ion exchange with STOR

| T (°C) | 1/T (K⁻¹) | [M⁺⁺] (mg/L) | (pH)ₐ | [H⁺]ₐ (mol/L) | (pH)ₜ | [H⁺]ₜ (mol/L) | [H⁺] (mol/L) | [H⁺] (mg/L) | K (mg/L) |
|--------|------------|--------------|--------|---------------|--------|---------------|--------------|--------------|----------|
| 29     | 0.0033     | 50           | 6.31   | 4.898 x 10⁻⁷  | 1.42   | 0.0380        | 0.0380       | 38.0189     | 28.9088  |
| 40     | 0.0032     | 50           | 6.31   | 4.898 x 10⁻⁷  | 1.48   | 0.0331        | 0.0331       | 33.1131     | 21.9296  |
| 50     | 0.0031     | 50           | 6.31   | 4.898 x 10⁻⁷  | 1.51   | 0.0309        | 0.0309       | 30.9030     | 19.0999  |
| 60     | 0.0030     | 50           | 6.31   | 4.898 x 10⁻⁷  | 1.61   | 0.0245        | 0.0245       | 24.5471     | 12.0512  |

Table 6. Equilibrium constant (K) for the copper ion exchange with STOR

| T (°C) | 1/T (K⁻¹) | [M⁺⁺] (mg/L) | (pH)ₐ | [H⁺]ₐ (mol/L) | (pH)ₜ | [H⁺]ₜ (mol/L) | [H⁺] (mol/L) | [H⁺] (mg/L) | K (mg/L) |
|--------|------------|--------------|--------|---------------|--------|---------------|--------------|--------------|----------|
| 29     | 0.0033     | 50           | 6.48   | 3.311 x 10⁻⁷  | 1.39   | 0.0407        | 0.0407       | 40.7380     | 33.1917  |
| 40     | 0.0032     | 50           | 6.48   | 3.311 x 10⁻⁷  | 1.45   | 0.0355        | 0.0355       | 35.4813     | 25.1785  |
| 50     | 0.0031     | 50           | 6.48   | 3.311 x 10⁻⁷  | 1.52   | 0.0302        | 0.0302       | 30.1995     | 18.2402  |
| 60     | 0.0030     | 50           | 6.48   | 3.311 x 10⁻⁷  | 1.57   | 0.0269        | 0.0269       | 26.9153     | 14.4887  |

Table 7. Equilibrium constant (K) for the nickel ion exchange with STOR

| T (°C) | 1/T (K⁻¹) | [M⁺⁺] (mg/L) | (pH)ₐ | [H⁺]ₐ (mol/L) | (pH)ₜ | [H⁺]ₜ (mol/L) | [H⁺] (mol/L) | [H⁺] (mg/L) | K (mg/L) |
|--------|------------|--------------|--------|---------------|--------|---------------|--------------|--------------|----------|
| 29     | 0.0033     | 50           | 6.60   | 2.512 x 10⁻⁷  | 1.35   | 0.0447        | 0.0447       | 44.6684     | 39.0525  |
| 40     | 0.0032     | 50           | 6.60   | 2.512 x 10⁻⁷  | 1.40   | 0.0398        | 0.0398       | 39.8107     | 31.6979  |
| 50     | 0.0031     | 50           | 6.60   | 2.512 x 10⁻⁷  | 1.46   | 0.0347        | 0.0347       | 34.6737     | 24.0453  |
| 60     | 0.0030     | 50           | 6.60   | 2.512 x 10⁻⁷  | 1.54   | 0.0288        | 0.0288       | 28.8403     | 16.6353  |

Table 8. Equilibrium constant (K) for the cobalt ion exchange with STOR

| T (°C) | 1/T (K⁻¹) | [M⁺⁺] (mg/L) | (pH)ₐ | [H⁺]ₐ (mol/L) | (pH)ₜ | [H⁺]ₜ (mol/L) | [H⁺] (mol/L) | [H⁺] (mg/L) | K (mg/L) |
|--------|------------|--------------|--------|---------------|--------|---------------|--------------|--------------|----------|
| 29     | 0.0033     | 50           | 6.71   | 1.950 x 10⁻⁷  | 1.33   | 0.0468        | 0.0468       | 46.7735     | 43.7552  |
| 40     | 0.0032     | 50           | 6.71   | 1.950 x 10⁻⁷  | 1.38   | 0.0417        | 0.0417       | 41.6869     | 34.7560  |
| 50     | 0.0031     | 50           | 6.71   | 1.950 x 10⁻⁷  | 1.45   | 0.0355        | 0.0355       | 35.4813     | 25.1785  |
| 60     | 0.0030     | 50           | 6.71   | 1.950 x 10⁻⁷  | 1.52   | 0.0302        | 0.0302       | 30.1995     | 18.2402  |
Table 9. Thermodynamic parameters for CTOR and STOR

| Metal Ion | CTOR | STOR |
|-----------|------|------|
|           | \(\Delta H\) (kJ/mol) | \(\Delta S\) (J/K/mol) | \(\Delta G\) at 29°C (kJ/mol) | \(\Delta H\) (kJ/mol) | \(\Delta S\) (J/K/mol) | \(\Delta G\) at 29°C (kJ/mol) |
| Zinc      | -18.378 | -36.430 | -7.376 | -22.972 | -47.648 | -8.583 |
| Copper    | -20.292 | -41.407 | -7.787 | -23.356 | -47.993 | -8.862 |
| Nickel    | -21.058 | -42.862 | -8.113 | -24.121 | -48.682 | -9.420 |
| Cobalt    | -22.590 | -46.538 | -8.536 | -24.504 | -49.218 | -9.640 |

4. CONCLUSION

This study has demonstrated that the use of orange mesocarp extract as a substitute for phenols in the production of cation exchange resins is feasible. Results from batch experiments showed that factors such as pH and temperature affect the ion exchange capacity. The equilibrium of the ion exchange process was based on the law of mass action, and the maximum metal ion exchange occurred at 29°C. Thermodynamic data analysis indicated that the ion exchange process is spontaneous, exothermic and of negative entropy. Experimental results revealed that the ion exchange capacity is in the order: STOR > CTOR, which is of similar trend with their dissociation strength. However, 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 successful application of CTOR and STOR in waste-water treatment plant will help in recycling orange mesocarp wastes and removal of metal ions thereby making the environment friendly and also provide a good local substitute for imported ion exchange resins thus conserving foreign exchange earnings.
COMPETING INTERESTS

Authors have declared that no competing interests exist.

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