



Sorption Mechanism of Metal Ions Uptake from Aqueous Medium by Chemically Modified Red Onion (*Allium Cepa*) Skin Extract

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Abstract

The chemical modification of the polyhydroxylic extract of red onion skin to yield carboxylated-epichlorohydrin red onion skin extract resin (CERR) and its sorption behavior in the uptake of Mn^{2+} , Fe^{2+} and Pb^{2+} ions from aqueous medium was investigated. Metal ion uptake was evaluated at different particle sizes (≈ 63 to $500\ \mu m$), periods of agitation (2 to 60 mins) and temperatures (29 to $70^\circ C$) with 50 mg/L metal ion solution. The optimal particle size was found to be $\approx 150\ \mu m$, while the percentage exchange for the metal ions was in sequence ($Mn^{2+} > Fe^{2+} > Pb^{2+}$) which is consistent with their ionic radii. The percentage metal ion uptake increased with time, and reached equilibrium at 86.69 % (Mn^{2+}) from 35mins; 77.01 % (Fe^{2+}) and 66.34 % (Pb^{2+}) from 40mins. The percentage metal ion exchange reduced with temperature increase in the range of 29 to $70^\circ C$, suggesting better performance with CERR at $29^\circ C$. Examination of the mechanism of uptake of metal ions using CERR was conducted with Dubinin-Radushkevich isotherm model. Computed values of mean free energy are 8.500, 8.181 and 8.248 kJ/mol for Mn^{2+} , Fe^{2+} and Pb^{2+} ions respectively, which corresponds to ion exchange as the dominant mechanism.

Keywords: Chemical modification, Red onion skin, Ion exchange, Dubinin-Radushkevich model, Metal ions, Resin.

Introduction

The red onion (*Allium cepa*) bulb is a flavorful round-layered vegetable which consists of fructans (micro units of carbohydrate molecule that support gastrointestinal health by sustaining beneficial bacteria), flavonoids (antioxidants which render molecules that are dangerous to the body cells inactive) and organosulfur compounds (components that give the onion its taste and smell)¹. The edible part of onion and its outer dry layer have exhibited great potential benefits in food, color and medicinal chemistry from time immemorial. The observation in some scholarly research on the characterization of extract of dry papery skin of red onion revealed the presence of components like anthocyanin (using acetate and phosphate buffer solutions as extractant)²; flavonols, flavones and anthocyanidines (using water as extractant)³; and mixed hydrolysable and condensed tannins (using acetone as extractant)⁴. These findings indicate that the extract of red onion skin (an abundant agro waste) consists of polar hydroxyl groups which could enhance its susceptibility to chemical modification⁵⁻⁸. Chemical modification involves the variation of bonds, ions, atoms, radicals and molecules within the skeletal frame of a compound through chemical means; or the incorporation of bonds, ions, atoms, radicals and molecules through synthesis with chemical reagents to form an expanded structure of the original compound. These changes at localized portions of the initial moiety are intended to: i. Tailor the characteristic property of the original substance for targeted application, ii. Maintain the formulated product in its eco-compatible state, iii. Better the microbe-resistance capability of the sorbent, iv. Be supportive

during process operations in order to conserve energy, v. Sustain temperature conditions manageability of the reactant system, vi. Maximize the functionality of the active groups of the sorbent in the binding of ions, vii. Positively influence the feasibility and reactant rate of the process with time, viii. Yield sorbents with long-lasting shelf life, ix. Adjust the water retention and repellency attributes of the sorbent, in a way that makes the geometry of the molecule more stably patterned, x. Upgrade the quality of sorption process and strengthen the overall economy of its application.

The contamination of fresh water by the discharge of inadequately treated effluents from agricultural, industrial and domestic activities, coupled with providing appropriate measures to forestall problems of toxic discharges and prevent the long term negative impact on aquatic and terrestrial lives, are the challenges facing researchers, environmentalists, industrialists, pollution control and management agencies the world over⁹⁻¹³. The need therefore, arises to develop sorbents that are structurally biodegradable, ecologically compatible and economically feasible for application in effluent treatment plants. The mode of sorption by carboxylated-epichlorohydrin red onion skin extract resin (CERR) with regards to Mn^{2+} , Fe^{2+} and Pb^{2+} ions from aqueous medium was investigated. In the aqueous environment, the sequence of steps in sorption reaction is centered on the directional flow of associated energy, forces, exchangeable and exchanging charged particles across the functional sites located at the permeation of pores within the resin molecule. This presentation is concerned with assessing the influence of particle size, time and temperature on the

uptake of Mn^{2+} , Fe^{2+} and Pb^{2+} ions from aqueous solution by chemically modified extract of red onion skin; as well as resolves the mechanism of sorption which is vital for the efficient management of the operational design of a large-scale water treatment plant.

Materials and Methods

Sample Collection and Preparation: Red onions were obtained from the fruit garden market in Port Harcourt, Nigeria for the purpose of this study. The outermost skin was carefully stripped and dried for 3 days at 29°C after washing with deionised water. The dried red onion skin was pulverized with an electric milling machine, sieved to 150 μm particle size and stored in tightly capped plastic bottle at 29°C.

Extraction Procedure: The extraction process was carried out with 2940 g of 150 μm size red onion skin and acetone (extracting solvent) using soxhlet extractor. Rotor evaporator was used to recover the extracted sample from the acetone-extract mixture.

Formulation of Carboxylated-Epichlorohydrin Red Onion Skin Extract Resin (CERR): 10 ml of epichlorohydrin was poured into a beaker containing 17.3 g of 4-hydroxy-benzoic acid in 70 ml acetone) and vigorously stirred. 38 g sample of the extract (dispersed in 180 ml of acetone) was added to the mixture and the beaker with its content placed on a heating mantle. The beaker was gently heated at 60°C, with the content constantly stirred until the mixture turned into a brown coloured slurry in about 3 hours, which solidified after 15 minutes. After 20 hours, the mass of the resin was then crushed, sieved to obtain different particle sizes and preserved in corked bottles at 29°C.

Standard solution preparation: The 1000 mg/l metal ion stock solutions were each prepared in 1litre volumetric flask by dissolving 3.0785 g of $MnSO_4 \cdot H_2O$, 4.973 g of $FeSO_4 \cdot 7H_2O$ and 1.59 g of $Pb(NO_3)_2$ in distilled deionised water. Working standard solutions of 50 mg/l Mn^{2+} , Fe^{2+} and Pb^{2+} ions were obtained by dilution. Analytical grade reagents were used for the experiments.

Sorption studies: The sorption experiments were performed by shaking the tightly capped conical flask containing 1g of CERR and 50 cm^3 of 50 mg/l metal ion solution at 120 oscillations / min. The mixture was centrifuged and filtered through glass wool after 1hour of shaking at 29°C. The concentration of metal ion in solution was determined by analysing the clear filtrate using the Atomic Absorption Spectrophotometer (Perkin Elmer, Analyst 200). Systematic batch experiments were conducted as described above with initial metal ion concentrations of 50 mg/l at varying particle sizes (≈ 63 to 500 μm), agitation time (2 to 60 mins) and temperature range of 29 to 70°C. Evaluation of percentage metal ion exchange (M_E) at varying temperatures were carried out using Equation (1) and the values plotted as a

function of temperature¹⁴.

$$M_E = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

The ion exchange capacity (q_e) of CERR was ascertained by the mass balance from initial to equilibrium compositions using the relationship in equation (2) and the values plotted against those of initial metal ion concentration¹⁵.

$$q_e = \frac{V}{m} (C_o - C_e) \quad (2)$$

Where: C_o and C_e are the initial and equilibrium metal ion concentrations in solution (mg/l) respectively, V is volume of initial metal ion solution used (l), and m is mass of CERR used (g).

Results and Discussion

Influence of Particle Size: The influence of varied sizes (≈ 63 , 150, 250, 300, 400 and 500) μm of CERR particles on the percentage exchange was experimented at 29°C and 200 rpm with 50 mg/l of the Mn^{2+} , Fe^{2+} and Pb^{2+} ions solution for 60 mins agitation time. The results of the percentage exchange are shown in Figure-1.

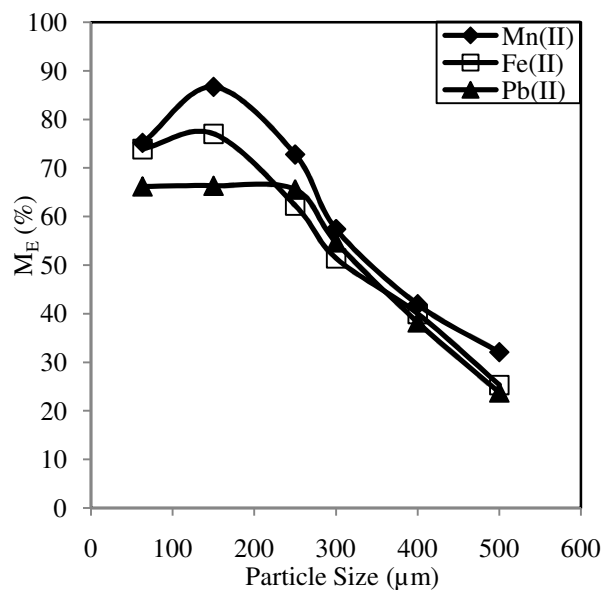


Figure-1
Plot of percentage metal ion exchange as a function of resin particle size

The pattern of plots in this figure reflect slight increase in percentage exchange from ≈ 63 to 150 μm size, and steady decrease (from 86.69 to 39.02 % for Mn^{2+} , 77.02 to 25.31 % for Fe^{2+} and 66.34 to 23.79 % for Pb^{2+} ions) beyond $\approx 150 \mu m$. In

considering the percentage exchange of CERR particles with the larger sizes, it seems as though some pores leading to ion exchange sites are encased within the coarse particulate, thereby locking access of the diffusing metal ions to these areas. Again, this enclosure of channels could create some sort of exchange barrier which is likely to retard or even cause redundancy in the activity of those sites, and in turn lower the degree of percentage exchange of the larger sized CERR. On the other hand, the higher degree of percentage exchange for CERR particles of ≈ 63 and $150\ \mu\text{m}$ sizes signifies exposure and better positioning of greater number of interaction points on the particulate molecules per unit area as compared to relatively larger size CERR molecules in which some of the reactive points are embedded within the resin lattice. The increase in percentage exchange with decrease in particle size possibly conforms to more effective contact between the $50\ \text{mg/L}$ exchanging ions and the greater quantity of ion exchange active points on the smaller particle sized CERR surface.

Effect of Agitation Time: The variance in percentage exchange of $50\ \text{mg/L}$ metal ion solution at 29°C with agitation time is depicted in Figure-2.

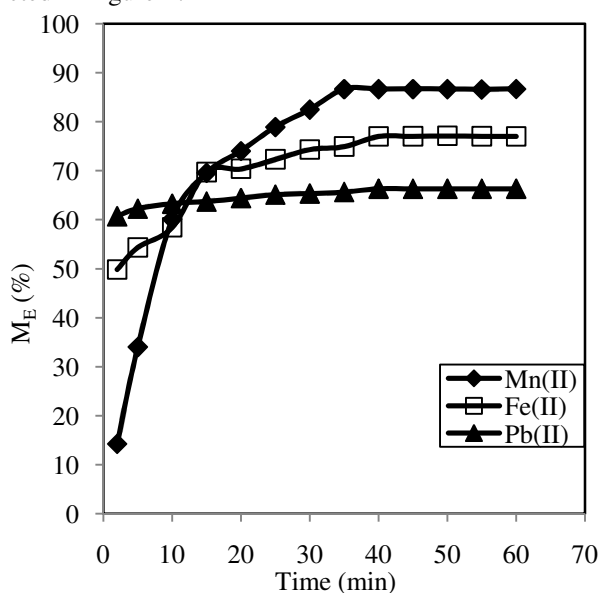


Figure-2

Plot of percentage metal ion exchange at different agitation times

The plots showed steady increase in the metal ions uptake (from 14.25 to 74.05% within 2 to 20 mins, and in 35mins got up to 86.69 % for Mn^{2+} ; 49.85 to 69.71% within 2 to 15 mins, and in 40mins got up to 77.01 % for Fe^{2+} ; and 60.74 to 64.41% within 2 to 20 mins, and in 40mins got up to 66.34 % for Pb^{2+}). This progressive increase at the initial stage could be attributed to the unoccupied active and accessible sites of CERR which enhanced rapid interaction between the exchanging metal ions and exchangeable ions on the resin. With further increase in agitation period, only a fraction of the metal ions that migrate to

the interior sites are exchanged due to repulsion between metal ions occupying the exchanger surface and that in solution phase as demonstrated by relatively small increase in percentage metal ions uptake (from 20 to 35mins for Mn^{2+} , 15 to 40mins for Fe^{2+} and 20 to 40mins for Pb^{2+}). After these times of agitation, no remarkable change in the percentage exchange was observed as illustrated by the plateau region of the time dependency graph in Figure 2. This suggests the time for attainment of equilibrium. The trend of the rate of attainment of equilibrium for the metal ions, is in line with their ionic radii (0.67 , 0.78 and $1.21\ \text{\AA}$ for Mn^{2+} , Fe^{2+} and Pb^{2+} ions respectively)¹⁶. In the use of acrylic-modified sugarcane bagasse for the retrieval of metal ions from aqueous solution, the equilibrium time for adsorption was achieved in 60mins for Pb^{2+} , 90mins for Cd^{2+} and 180mins for Cu^{2+} ions. The Pb^{2+} adsorption rate was much higher suggesting that the process may be dominated by chelation due to the polymeric super hydrophilic network and an abundance of $-\text{COO}^-$ and $-\text{NH}_2$ groups in the sugarcane bagasse-based hydrogels¹⁷.

Effect of temperature: Proper monitoring of working temperature enhances the efficiency of ion exchange process and helps in averting alterations in some operating factors like degree of ionization, diffusion rate of ions, solubility of ions, conductivity of ions, relative affinity of ions, rate of hydrolysis, viscosity of the medium, chemical potential, etc.. The results of percentage exchange at temperatures of 29, 40, 50, 60 and 70°C are represented in Figure-3.

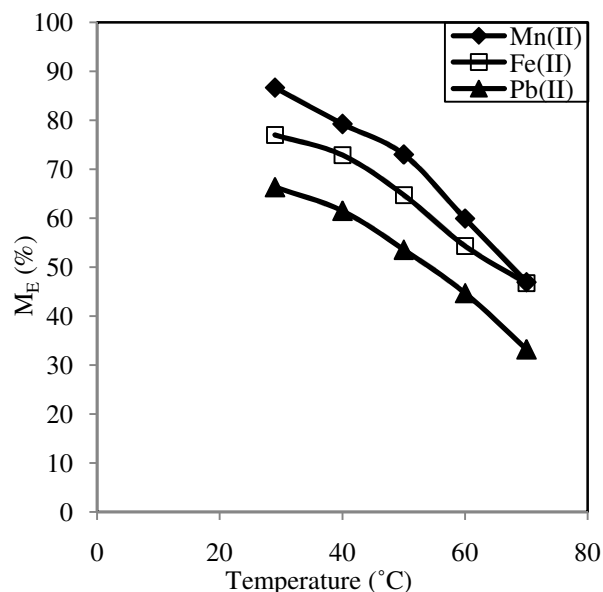


Figure-3

Plot of percentage metal ion exchange at different temperatures

For the metal ions studied, a decrease in percentage exchange (from 86.69 to 46.92 % for Mn (II), 77.02 to 46.74 % for Fe (II) and 66.34 to 33.23 % for Pb (II) ions) with temperature increase

in the range of 29 to 70°C was observed. This decrease is attributable to the shrinking, clumping and blinding of the internal pores of the CERR particles as temperature is increased. It is likely that these changes may have introduced unfavorable condition within the system which affected the size distribution, spatial orientation and effective performance of the active functional group of the CERR molecule, thereby decreasing the percentage exchange. Again, it could be that increase in temperature decreased the percentage exchange, possibly as a result of weakening of forces of interaction between the metal and exchangeable H^+ ions, and thus driven in the direction that led to the slip away of metal ions from the CERR surface to the solution medium. In the present investigation, the CERR molecule is characterized by the carboxyl functional group and therefore could be classified as weak acid cation exchange resin^{18,19}. This implies that it ionizes partially and is sparingly soluble in aqueous system. It could then be that increase in temperature, increased its solubility and the degree of ionization, resulting in the lowering of the chemical potential of the process. These effects apparently caused reduction in the relative affinity of the metal ion for H^+ ions, leading to a decrease in the percentage exchange on the CERR. Similar observation of increase in temperature resulting to decrease in adsorption efficiency of Pb (II) ions was recorded; indicating the process to be exothermic, since lower temperatures favored the process of adsorption²⁰. The removal of Pb^{2+} and Cd^{2+} ions by rice husk ash in the presence of anionic micelles showed that the adsorption capacity increased within the experimental temperature of 25 to 60°C, which signifies the uptake process to be potentially endothermic²¹.

Sorption studies: The Dubinin-Radushkevich (DR) model which assumes a heterogeneous surface was employed in analyzing the experimental data at different temperatures so as to unravel the metal ion uptake mechanism. The linearized form of DR equation is expressed as equation 3:

$$\ln q_e = \ln q_D - B_D \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \quad (3)$$

Where: $[RT \ln (1 + 1/C_e)]$ is the Polanyi potential, q_D is the maximum ion exchange capacity, R is gas constant, T is temperature (29°C), B_D is the DR model constant and E is the mean free energy of sorption per mole of metal ion deduced with the formula²²:

$$E = \frac{1}{\sqrt{2B_D}} \quad (4)$$

The sorption mechanism is dominated by physisorption if the value of E is less than 8 kJ/mol, ion exchange if between 8 and 16 kJ/mol and particle diffusion if more than 16 kJ/mol²³. DR isotherm plots of $\ln q_e$ against the square of $[RT \ln (1 + 1/C_e)]$

for the removal of Mn^{2+} , Fe^{2+} and Pb^{2+} ions by CERR are linear as presented in Figure-4.

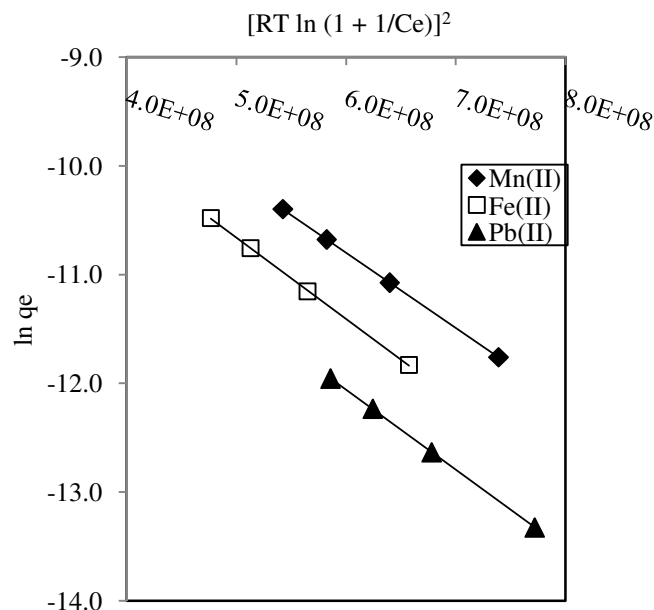


Figure-4
Dubinin-Radushkevich equation isotherms for the metal ions

The slopes and intercepts from Figure-4 were utilized to deduce B_D and q_D values, while E values were evaluated by substituting the values of B_D into equation 4 and presented in Table-1. The data for E suggests the predominance of ion exchange mechanism since the values are between 8 and 16 kJ/mol. Earlier studies on sorption of metal ions by unmodified orange mesocarp extract reported E value of 0.1581 kJ/mol which signifies physisorption, while that by modified orange mesocarp extract is between 8.452 and 11.180 kJ/mol, indicating ion exchange mechanism²⁴. The proposed mechanism of exchange of metal ion for hydrogen ions on CERR is presented in Figure-5.

Table-1
Dubinin-Radushkevich (DR) parameters for metal ion uptake with CERR

DR parameters	CERR		
	Mn^{2+}	Fe^{2+}	Pb^{2+}
Linear equation	$-6.919E-09x - 6.647$	$-7.470E-09x - 6.926$	$-7.355E-09x - 7.646$
q_D (mol/g)	1.294×10^{-3}	9.780×10^{-4}	4.760×10^{-4}
B_D (mol ² /J ²)	6.92×10^{-9}	7.47×10^{-9}	7.35×10^{-9}
E (kJ/mol)	8.500	8.181	8.248

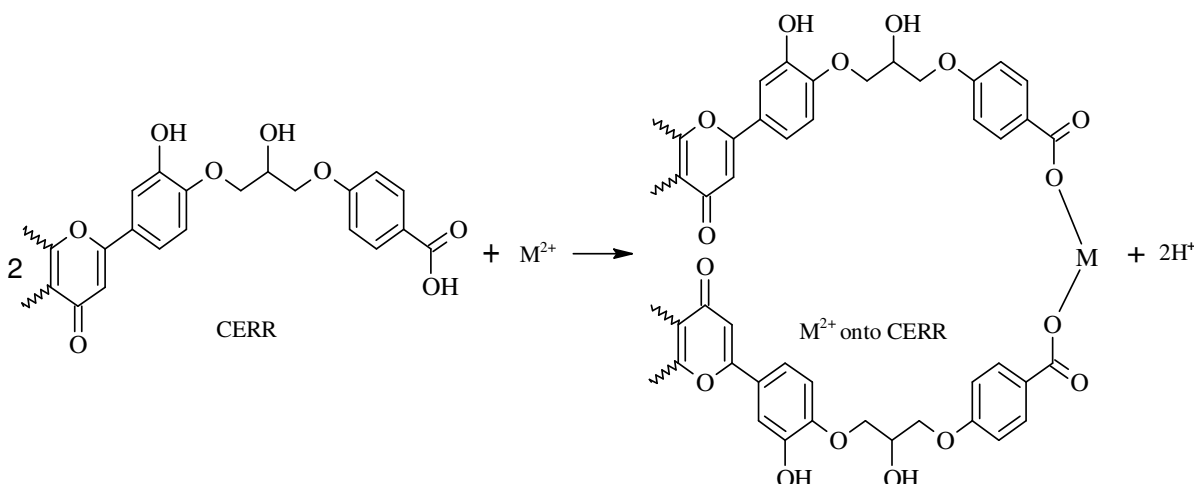


Figure-5
Proposed mechanism of exchange of metal ion (M^{2+}) for hydrogen ions (H^+) on CERR

Conclusion

The findings from this study have revealed the application of polyphenolic extract of red onion skin in the synthesis of exchange resin for the uptake of Mn^{2+} , Fe^{2+} and Pb^{2+} ions from aqueous medium. The CERR particle size and period of agitation influenced the exchange reaction. The percentage metal ion uptake increased steadily with time at the initial stage; and thereafter, the values remained relatively constant from about 35 mins for Mn^{2+} , and 40 mins for Fe^{2+} and Pb^{2+} ions. The percentage metal ion exchange reduced with temperature increase in range of 29 to 70°C, with the optimal exchange occurring at 29°C. DR data showed that metal ions removal with CERR occurred by ion exchange mechanism, with values of the mean free energy as 8.500, 8.181 and 8.248 kJ/mol for Mn^{2+} , Fe^{2+} and Pb^{2+} ions respectively.

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