

Utilization of Red Onion Skin Extract for Remediation of Lead (II) and Cadmium (II) Ions from Aqueous Solution

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ABSTRACT

This paper reports the utilization of modified and unmodified red onion skin extract in the removal of lead (II) and cadmium (II) ions from aqueous solutions using red onion skin extract. The extract was modified with maleic acid, succinic acid, citric acid and phosphoric acid. The modified and unmodified extracts were subjected to infra red spectral analysis. Studies on the efficiency of the extracts in metal ion removal showed that the percentage lead ion removal of the extracts increased from 85.85% for the unmodified red onion skin extract (UROSE), to 96.76, 97.81, 98.60 and 99.90 % for phosphoric acid modified red onion skin extract (PROSE), citric acid modified red onion skin extract (CROSE), maleic acid modified red onion skin extract (MROSE) and succinic acid modified red onion skin extract (SROSE) respectively. Percentage removal of cadmium (II) ions increased from 59.3 % for UROSE to 75.95 % for MROSE, 92.00 % for CROSE, 94.00 % for PROSE, and 98.45 % for SROSE. Generally, the exchange capacity for the modified and unmodified extracts was higher for lead (II) ions than for cadmium (II) ions. The result obtained from the study indicated that SROSE has the highest exchange capacity of all the modified extracts. These results have demonstrated that modification of red onion skin extract increases its metal ion removal capacity. Thus, modified and unmodified red onion skin extract can serve as effective, renewable, low cost source of ion exchangers for the remediation of lead (II) ions and cadmium (II) ions contaminated waste water.

Keywords: Red onion skin extract, lead, cadmium, exchange capacity.

1.0 INTRODUCTION

Heavy metal contamination of aquatic ecosystems has developed into a global environmental and public health issue. This is because, these heavy metal are persistent, not metabolized to other intermediate compounds, bio accumulate and do not easily breakdown in the environment (Raikwar, 2008). Lead and cadmium are among heavy metals which have attracted a lot of attention due to their high level of toxicity. Lead occupies the first position in the United States agency for toxic substances (ASTDR), which lists all hazards present in toxic waste sites according to their prevalence and the severity of their toxicity, and cadmium occupies the sixth position (Hu, 2002). Thus, while some heavy metals like Fe, Mn, Mo, Ni, Zn and Cu are essential micronutrients required for normal growth and metabolic processes (Morsy et al., 2012), Cd and Pb are nonessential and highly toxic to plants (Sebastiani et al., 2004; Rai et al., 2004), and animals (Benaïssa, 2009; Rao, 2010).

One point source of cadmium and lead in our waterways is the discharge of lead and cadmium contaminated industrial effluents (produced water) from oil and gas exploration (Durell et al., 2000). Produced water contains a wide variety of constituents such as organic and inorganic pollutants, suspended solids, and iron (Igwe et al., 2013). The predominant contaminants in typical produced water are summarised in table 1.

Much research interest has been concentrated on the use of agricultural wastes in both their modified and unmodified forms as effective, inexpensive and renewable source of sorbents for the removal of heavy metals from aqueous solutions. However, these biosorbents need further modifications to increase their active binding sites and also make them readily available for sorption (Popuri et al., 2007).

Table 1: Major Contaminants of Produced Water.

S/NO	Contaminant	Examples
1	Dissolved organic compounds	<ul style="list-style-type: none"> • Fatty acids • Polar Organic (phenol, aldehyde) • Non Polar Organic (aliphatic, aromatic)
2	Process chemicals	<ul style="list-style-type: none"> • Corrosion control: amide imidazoline compound • Scale control: phosphate ester/phosphate compounds • Emulsion breaking: oxyalkylated resins/polyglycol ester/alkylarylsulfonates • Dehydration of natural gas: methanol/glycol
3	Heavy metals and radioactive materials	<ul style="list-style-type: none"> • Cadmium, chrome, copper, lead, mercury, nickel, radium, silver and zinc
4	Suspended solids	<ul style="list-style-type: none"> • Inorganic: geological formation (siliceous and calcareous) • Sparingly soluble inorganic salts: calcium carbonate • Organic: ashphaltenes, paraffins, suspended oil • Microorganism: anaerobes (Sulfate Reducing Bacteria)

Source: Visvanathan, 1993; Murray-Gulde, 2003

Modified agricultural wastes like peanut and walnut shells (Johns et al., 1998), maple saw dust (Yu et al., 2001), soybean hull (Marshall and Wartelle, 2003), corn cob (Leyva-Ramos, 2005; Nada, 2009), flax and cotton fibre (Marshall, 2006), orange mesocarp (Ogali et al., 2008), cellulose (Thanh and Nhung, 2009), banana peel, orange peel, maize tassel, onion skin and garlic skin (Annadurai, 2002; Zvinowanda, 2009; Chowdry et al., 2011) have all been investigated for their heavy metal removing capacities.

In the last five years, researchers are focussing more attention on the extraction and modification of the active phytochemical functional groups responsible for the metal removal properties of these agro-wastes. Ibezim-Ezeani et al., (2012) investigated the removal of zinc and other heavy metals using sulphonated and carboxylated orange mesocarp extract. Coconut coir dust extract modified with 4-hydroxybenzene carboxylic acid, phenol-4-sulphonic acid and toluenediisocyanate has also been utilized for removal of lead (Israel et al., 2013). Daneshfozoun et al. (2014) extracted cellulose from oil palm empty fruit bunches, modified with EDTA and acetic acid and utilized the modified product in the removal of Cu, Ni and Mn from aqueous solution. They discovered that EDTA modified cellulose had better sorption capacities than acetic acid modified cellulose.

This research was aimed at investigating the suitability of modified and unmodified extract from red onion (*Allium cepa*) skin in the removal of lead and cadmium ions from aqueous solution using batch adsorption techniques.

2.0 EXPERIMENTAL

2.1 Collection and Preparation of Onion Skin Sample

The onion skin used in this research was collected from Rumuokoro Market in Port Harcourt, Rivers State, Nigeria. The onion skin was sorted and air dried for two weeks, after which it was pulverized using an electric grinding mill.

2.2 Extraction of the Sample

The pulverized onion skin was subjected to extraction with acetone in a soxhlet extractor and the extract recovered from the extract-solvent mixture by evaporation.

2.3 Spectroscopic Analyses

Samples were prepared using the potassium bromide disc technique. The molecular structure of modified and unmodified red onion skin extract was investigated with a Fourier transform infrared (FTIR) system prestige 21 (Shimadzu), and the infrared absorption spectra recorded in the region of 4000 – 400 cm⁻¹.

2.4 Preparation of Modified Extracts

2.4.1 Preparation of Maleic Acid Modified Red Onion Skin Extract (MAMROSE)

The procedure was based on that described by Muhammad et al., (2009), with some modifications in temperature and time. The extract (15g) was dissolved in water (100 ml) at room temperature, on a magnetic stirrer for 30 minutes. To the stirred mixture was added maleic acid (2.86 g) and the temperature increased to 50°C. Iodine (0.152 g, 1.2mmol) was added to the mixture and heating continued on an oil bath with the temperature maintained at 50°C for 2 hrs. The reaction mixture was removed from heat and allowed to cool to room temperature. A saturated solution of Na₂S₂O₄ was added to the mixture until the brownish colour of the iodine turns colourless. The mixture was filtered and washed with deionised water (250 ml x 3), and the residue obtained dried for 4 hrs in an oven at 60°C and stored in airtight containers.

2.4.2 Preparation of Other Modified Extracts

The procedure outlined above was followed in the synthesis of the citric acid modified extract (CAMROSE), succinic acid modified extract (SAMROSE) and phosphoric acid modified extract (PAMROSE). The experimental condition for their synthesis is summarised in table 2.

Table 2: Experimental Condition for Molecular Iodine Catalysed Preparation of Modified Onion Skin Extract in Aqueous Medium

Modifying Agent	Sample Code	Mass of Modifying Agent (g) for 15 g Extract	Mass of Iodine (g)	Reaction Temperature (°C)	Time (h)
Maleic acid	MROSE	2.86	0.152	50	2
Citric acid	CROSE	2.85	0.24	50	4
Succinic acid	SROSE	4.00	0.152	50	2
Phosphoric acid	PROSE	3.25 (2.25ml)	0.02	80	1
Unmodified red onion skin extract	UROSE	-	-	50	4

2.4.3 Preparation of Unmodified Red Onion Skin Extract (UROSE)

The crude onion skin extract was dissolved in water (100 ml), at room temperature, on a magnetic stirrer for 30 minutes and the temperature increased to 50°C. It was heated at this temperature with constant stirring on a magnetic stirrer for 4 hrs.

2.5 Adsorption of Cadmium and Lead

0.3 g each of extract (both modified and unmodified) was soaked in 20 ml of each of the metal ion (Pb and Cd) solutions of initial concentration 20 mg/L. The suspensions were agitated for 1 h on a mechanical shaker (120 oscillations / min). The samples were then filtered and the filtrates were analysed using Atomic Absorption Spectrophotometer (AAS). The amount of the metal ions removed was obtained by the difference between the initial metal ion concentration and that of the supernatant.

The percentage of Pb²⁺ (or Cd²⁺) adsorbed on the adsorbent (P_e) was calculated by the following equation:

$$P_e (\%) = 100 \cdot \frac{C_o - C_e}{C_o} \quad (1)$$

The Pb²⁺ (or Cd²⁺) concentrations obtained were then used to calculate the absorption capacity, q_e (mg/g) of the adsorbent using the following mass balance equation:

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

where C_o, C_e, V, and M are initial Pb²⁺ or Cd²⁺ concentration (ppm), Pb²⁺ or Cd²⁺ concentration at equilibrium (ppm), the volume (L) of the solution and weight (g) of adsorbent, respectively.

3.0 RESULT AND DISCUSSION

3.1 Characterisation of Modified and Unmodified Extracts

The functional groups present in the modified and unmodified red onion skin extract were characterised by Fourier Transform Infrared (FTIR) spectrophotometry. The IR spectra of the modified and unmodified extracts are shown in figure 1. The spectra obtained were compared with previous literatures (Dyer, 1965; Heneczowski et al., 2001; Dehgham and Koshikam, 2010; Chourasiya et al., 2012) in order to identify them. The FTIR of UROSE showed some major peaks at $3450-3200\text{ cm}^{-1}$, 1693 cm^{-1} , 1600 cm^{-1} , 1504.48 cm^{-1} , 1467.83 cm^{-1} , 1317.38 cm^{-1} and 1207 cm^{-1} . The peak between 3450 and 3200 cm^{-1} is a characteristic absorption band for the OH and NH groups, the absorbance at 1693.5 cm^{-1} is assigned to the carbonyl stretch of a cyclic ketone. The peaks at 1600 cm^{-1} , 1504.48 cm^{-1} , 1467.83 cm^{-1} are typical of benzene containing compounds, while those appearing at 1317.38 cm^{-1} and 1207 cm^{-1} correspond to -C-OH deformations and phenolic OH vibrations respectively. These results are in agreement with report by Odozi et al (1986), stating that the red onion skin extract consist of polyhydroxyl phenols of the flavonoid type.

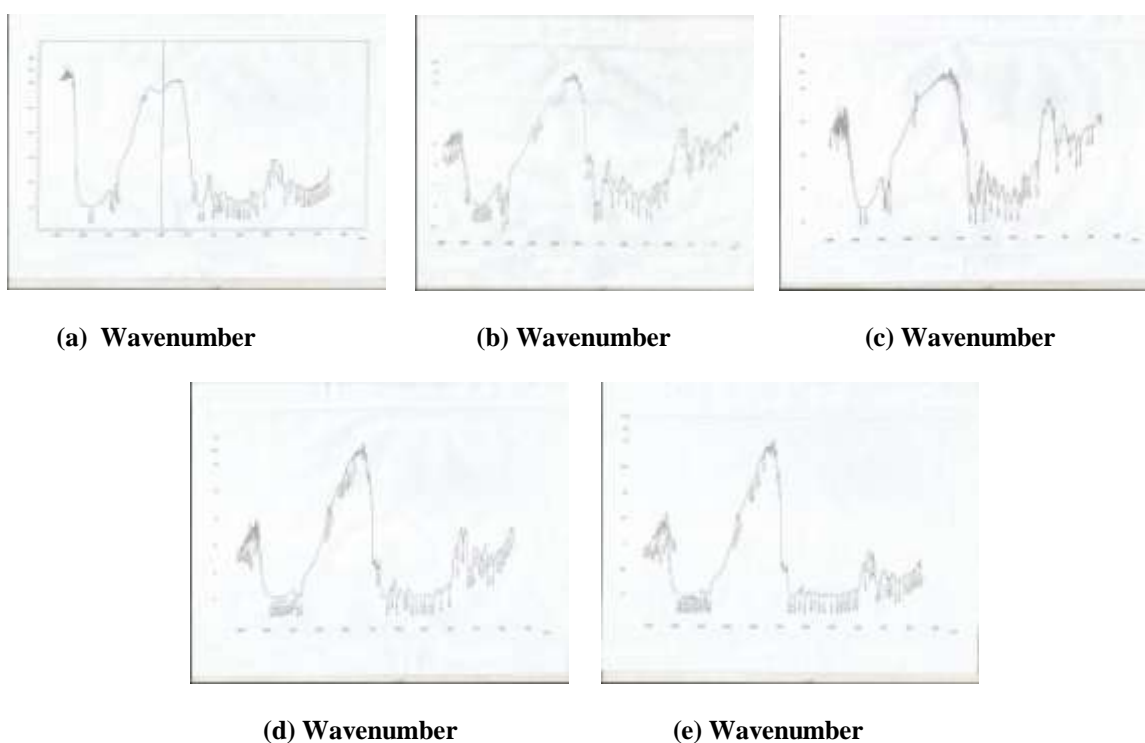


Fig. 1: IR Spectrum of (a) Unmodified Extract (b) SROSE (c) PROSE (d) CROSE (e) MROSE

Generally, there was no significant change in the appearance of the absorbance attributed to the OH group in CROSE and MROSE, while there was a shift towards higher wavelengths in PROSE and SROSE. Absorption peaks were observed in the spectra of SROSE, CROSE and MROSE at approximately 1701 cm^{-1} and 1734 cm^{-1} . These were attributed to the carbonyl stretching of an aliphatic ester and aliphatic carboxylic acid respectively. Beside the increased percentage transmittance of the absorption bands observed in the spectrum of PROSE, several sharp absorption peaks were observed at 1319.12 cm^{-1} , 1263.3 cm^{-1} and 1014.59 cm^{-1} . These were attributed to the P=O vibrations of trialkyl substituted phosphate esters, stretching vibrations of aryl – oxygen bond (Ar-O-P) and monoalkyl substituted phosphate esters (R-O-P=O). Two peaks characteristic of the phosphorus oxygen bond (P=O) vibrations were equally observed in the fingerprint region at 601.79 cm^{-1} and 638.44 cm^{-1} (Weast and Astle, 1981).

Table 3: Major Peaks in the FTIR Spectrum of Modified and Unmodified Red Onion Skin Extracts

FUNCTIONAL GROUP	ABSORPTION PEAK (cm^{-1})				
	UROSE	PROSE	SROSE	CROSE	MROSE
O-H stretching vibration of phenol	3450 -	3300.20 -	3238.48 -	3142-	3138 -

	3200	340822	3365.78	3375	3367.71
C=O stretch of aliphatic ester	-	-	1734.01	1734.01	1734.01
C=O stretch of aliphatic carboxylic acid	-	-	1701.2	1701.2	1701.2
C=O stretch of cyclic ketone	1693.5	1654.92	1653.00	1654.92	1649.00
C=C aromatic ring stretch	1600.92	1604.77	1600.92	1604.77	1600.92
C=C aromatic ring stretch	1504.48	1521.84	1500.62	1508.33	1512.19
	1467.83	1458.18	1448.54	1450.47	
	1369.46	1382.96	1375.25	1365.60	1363.67
- C-OH deformations	1317.38	1319.31	1319.31	1323.17	1319.31
C-O stretch of aryl ether	1273.02	1263.37	1269.16	1249.86	1273.02
C-O stretch of phenol	1207.41	1199.72	1199.72	1199.72	1201.65
C- CO-C stretching and bending of ketone	1165.00	1164.23	1165.00	1168.86	1166.93

3.2 Proposed Structure of Exchangers

The IR spectra indicated that the onion skin extract contains the polyhydroxyl phenol of flavonoid type, it is therefore proposed that crosslinking of the polyhydroxyl organic compounds in the extract by the di-carboxylic acids (succinic and maleic acids), tri-carboxylic acid (citric acid), and phosphoric acid, occurs through molecular iodine catalysed esterification reaction between the phenol in the extract and the carboxylic functional groups had occurred. This esterification reaction will not only polymerize the polyhydroxyl compounds in the extract but also insert carboxylic acid and phosphoric acid moieties into the molecules. Thus, citric acid will form a dianion extract citrate by reacting at a single site with the hydroxyl of the extract or at double sites to form the monoanion extract citrate. The formation of this and other modification products are illustrated in figures 2 – 5.

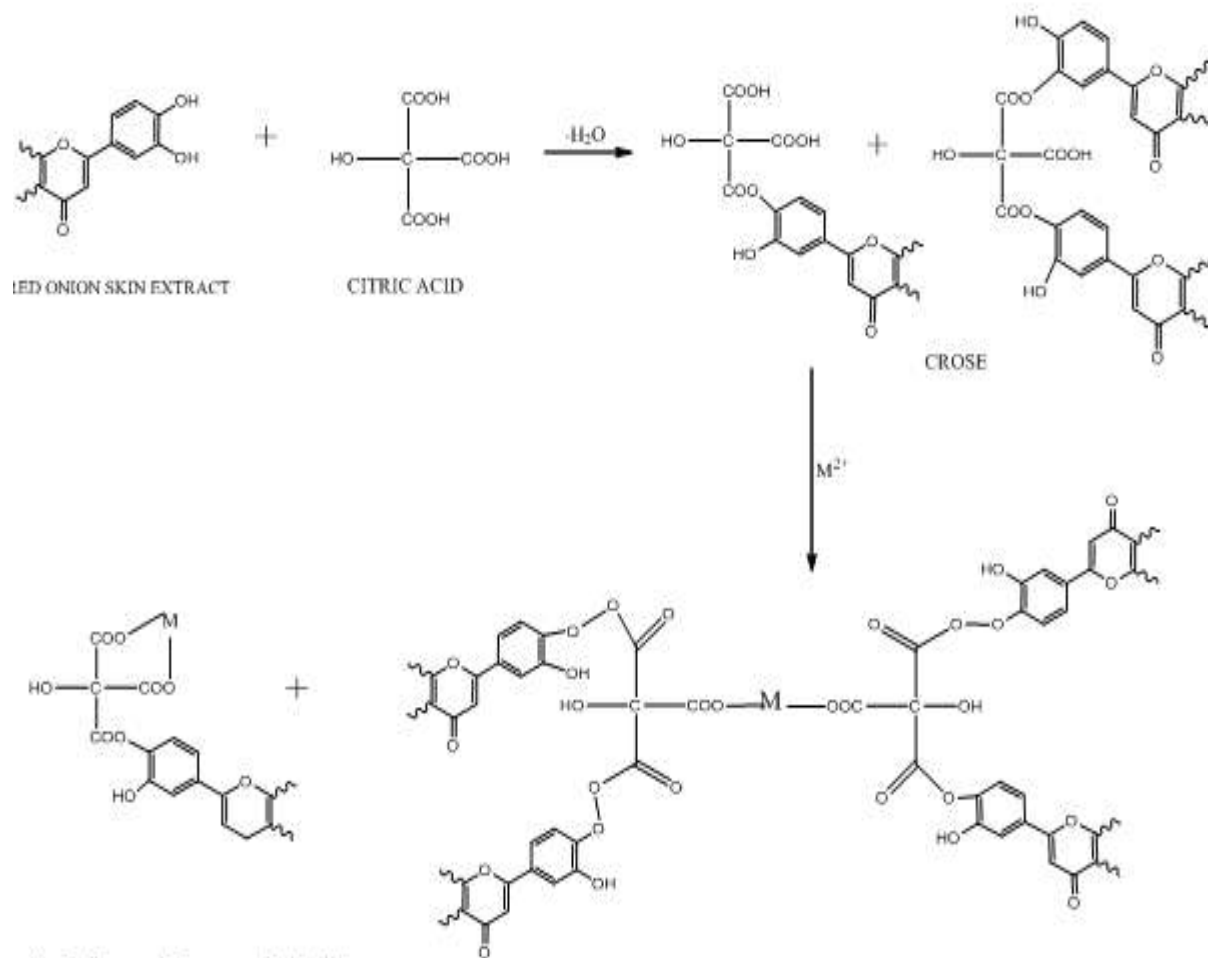


Fig. 2: Proposed structure of CROSE

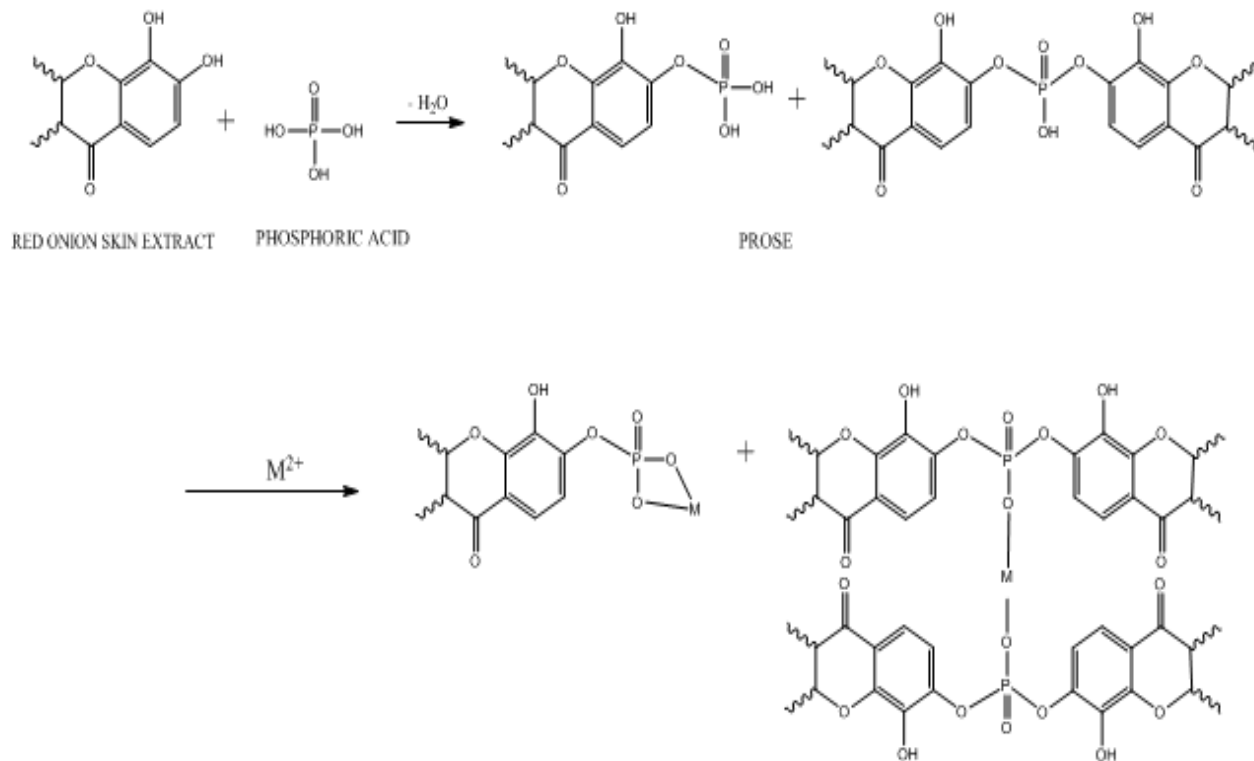


Fig. 3: Proposed structure of PROSE

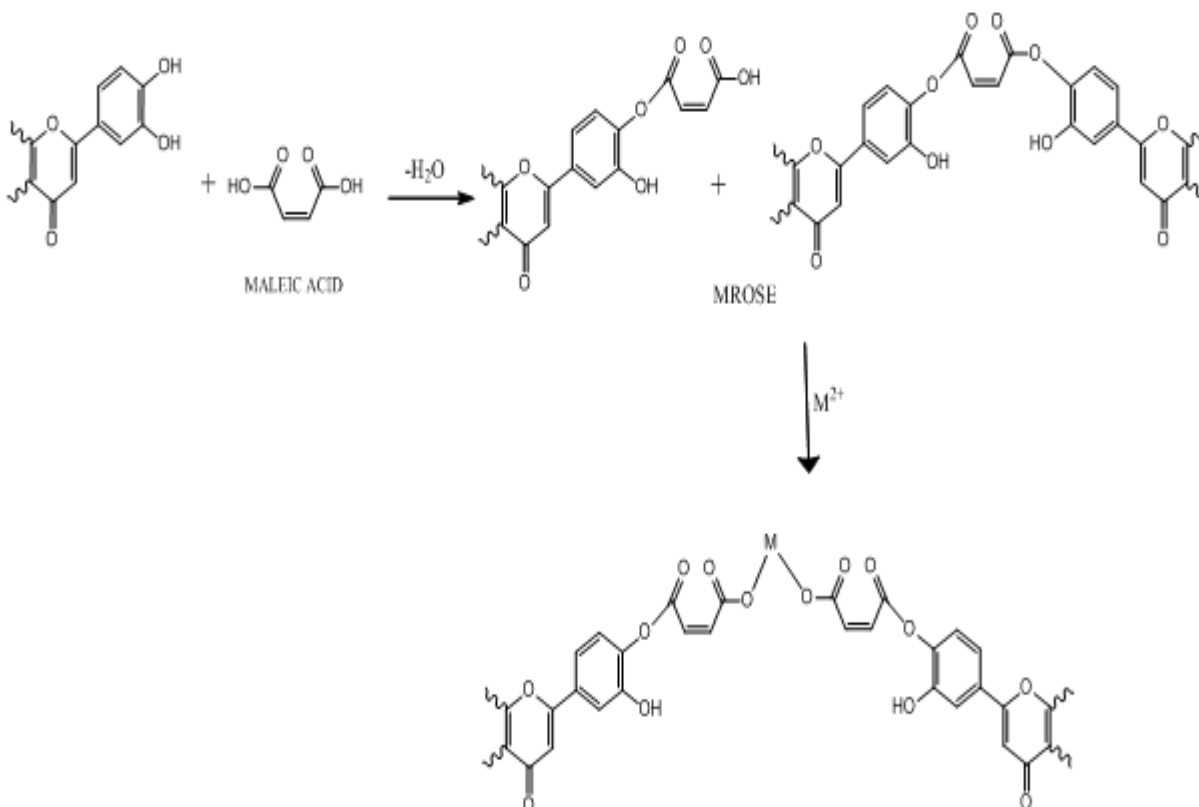


Fig. 4: Proposed structure of MROSE

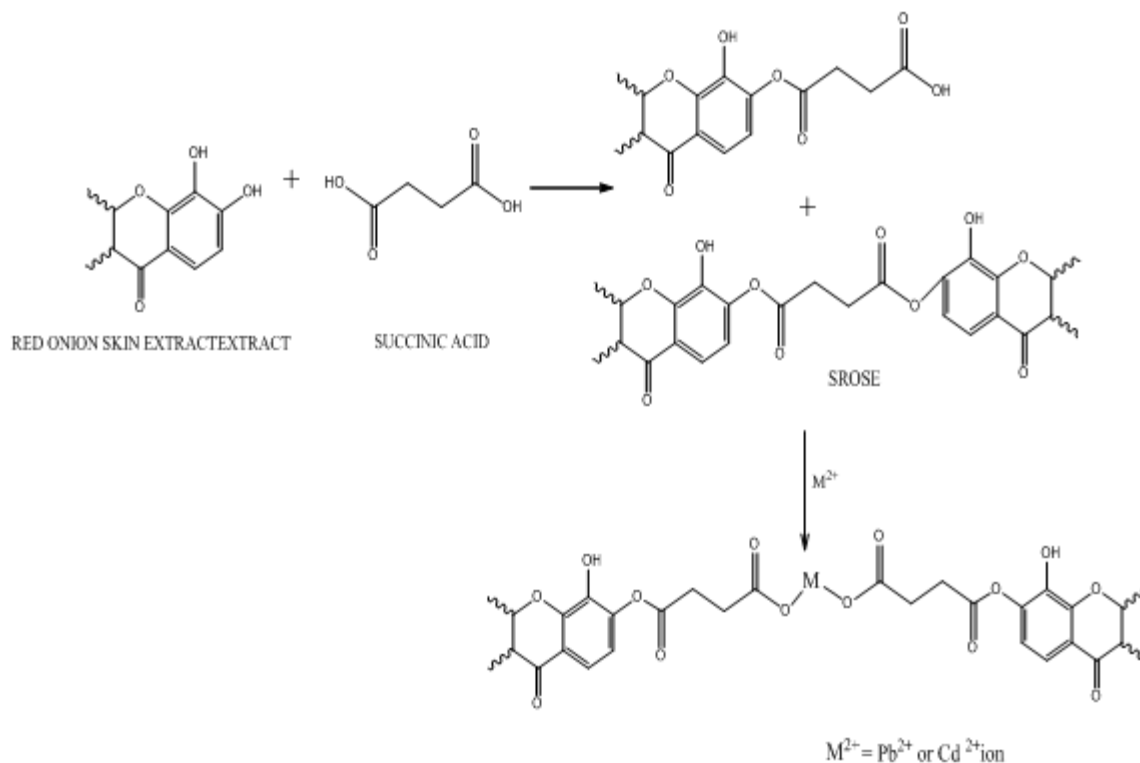


Fig. 5: Proposed structure of SROSE

3.3 Metal Ion Adsorption of Modified and Unmodified Red Onion Skin Extract

The summary of the metal ion adsorption analysis of the extracts is presented in Figure 6 and Table 4. Adsorption capacity and percentage removal of the red onion skin extract towards both Pb and Cd ions increased with the modification of the extract with the various modifying agents. From the results obtained, it was observed that both modified and unmodified extracts have a higher affinity for Pb (II) ions over and above Cd (II) ions under the same experimental conditions.

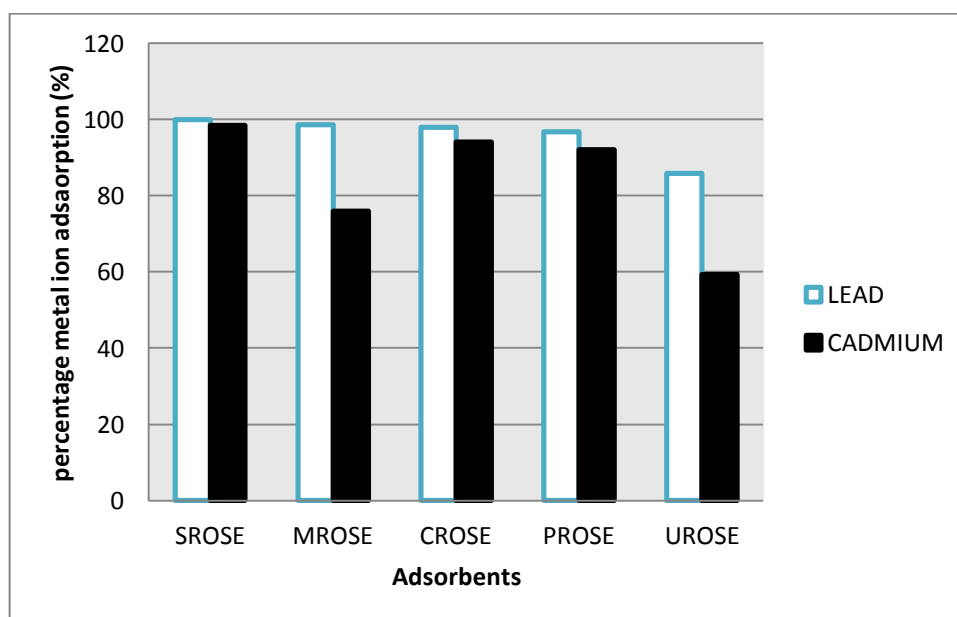


Fig. 6: Metal Ions Adsorption of Modified and Unmodified Red Onion Skin Extract

Table 4. Ion Exchange Capacity of the Extracts

SAMPLE CODE	ION EXCHANGE CAPACITY (mg/g)	
	LEAD	CADMIUM
MAMROSE	1.43	1.01
CAMROSE	1.45	1.31
SAMROSE	1.42	1.23
PAMROSE	1.34	1.25
UMROSE	1.26	0.79

The increase in metal ion uptake after modification is explained by the incorporation of carboxylic and phosphoric acid groups (Scheme 1 - 4) into the extract molecules. The pKa values of aliphatic carboxylic acids, monobasic phosphoric acid and dibasic phosphoric acid are 5.00, 7.21 and 2.12 respectively, while the pKa value of phenol is 9.80 (Weast and Astle, 1981). Since carboxylic and phosphoric acid groups are more acidic than phenols, their ion exchange capacities are higher relative to phenols.

CONCLUSION

Chemical treatment of red onion skin extract with maleic acid, succinic acid, phosphoric acid and citric acid increased their efficiency towards the removal of lead (II) and cadmium (II) ions from aqueous solution. The succinic acid modified red onion skin extract has the highest exchange capacity towards the removal of both lead (II) and cadmium (II) ions relative to maleic acid, citric acid and phosphoric acid treated extracts. Moreover, the selectivity of the modified and unmodified extracts for lead (II) ion is higher than that for cadmium (II).

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