

COMPARISON OF GEL AND MACROPOROUS RESINS USING THE REMOVAL OF Pb (II) IONS FROM AQUEOUS SOLUTIONS BY CATIONS EXCHANGE RESINS SYNTHESIZED FROM ORANGE MESOCARP AS CASE STUDY

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ABSTRACT

The gel and macroporous resins were compared using the removal of Pb(II) ions from aqueous solution by cation exchange resin synthesized from orange mesocarp. The resin synthesized from the orange mesocarp extract was observed to be a gel type resin while that synthesized from the orange mesocarp residue was observed to be a macroporous type resin. The experiment was carried out using 5ppm, 10ppm, 15ppm, 20ppm, and 25ppm solution of Pb(II) ion and 0.5g of the dry resin was added to 15ml of each concentration solution. Analysis using the atomic absorption spectrophotometer show 84.6% metal ion removal for the 5ppm solution orange mesocarp extract resin (gel type) and 41.0% metal ion removal for the 5ppm solution with the orange mesocarp residue resin (macro-porous type). The initial pH of the metal ion solution decreased from 6.8 to 1.5 for both resin. The result indicates that the orange mesocarp extract resin removed more metal ions at lower concentrations (5ppm) than the orange mesocarp residue resin.

Keywords: Gel Resin, Macroporous Resin, Lead Metal, Orange Mesocarp

INTRODUCTION

Over the years, ion exchange resins have been used both industrially and in laboratory research work as a means of separating mixtures and also for purification. However the quest for higher grade ion exchange resin had lead to continuous research in the area. Some industrial processes result in the release of heavy metals into the natural water systems. This has lead to an increasing concern about the effect of toxic metals as environmental contaminants. Lead pollutant is a major concern as lead has been used as industrial raw materials for storage battery manufacturing, printing, pigments, fuels, photographic materials and explosives manufacturing¹. Lead compounds are highly toxic to human. The presence of lead in drinking water even at very low concentration may cause such diseases as anemia, encephalopathy, hepatitis and nephritic syndrome². Thus, it is imperative that lead is removed from effluent before being discharged into the sewage system or into the aquatic environment³. An array of suitable methods exists for the removal of heavy metal pollutants from wastewater. These methods include precipitation, evaporation, electroplating and membrane separation. However, these methods have several disadvantages⁴. Ion exchange is one of the processes used for the removal of heavy metals from aqueous solution, but due to the high cost of purchasing the resin, the process has not been used extensively and effectively. Recently, agricultural waste has been used for the synthesis of ion exchange resin used for the removal of heavy metals from aqueous solutions.

When agricultural products are consumed, the remnants are left over and are usually disposed in most cases carelessly. Instead of littering the environment with these wastes, a lot a research

have been carried out and the results revealed that most agricultural waste contains important materials that could be used to synthesize ion exchange resins. For example orange (citrus sinensis) mesocarp is an agricultural waste containing rutin and cellulose which can be used to synthesize ion exchange resins. Other agriculture waste which have been investigated are walnut waste, peanut skin, cotton seed hulls, rice husk, palm kernel fiber, soya bean husk and other cellulosic material³. Rice husk as heavy metal adsorbent for the removal of lead (Pb^{2+}) from aqueous solution reveals that the optimum condition of Pb^{2+} uptake were initial concentration of 50.0mg/l, pH 5.0, biomass loading 0.2g and temperature of 60°C, and under such conditions, it was determined that the uptake was 8.60mg/g⁵. Palm kernel fibre was used as an absorbent for the removal of lead (II) ions from aqueous solutions. The report revealed that increasing the solution pH increases the percentage uptake of lead on the palm kernel fibre. Increase in the pH from 3 to 4 increased the percentage removal of Pb^{2+} by 33% for 90mg/dm³ solution, 27% for 50mg/dm³ solution and 26 for the 30mg/dm³ solution. Optimum Pb^{2+} removal was achieved at pH 5 for all three concentration of Pb^{2+} used⁶. Investigations on the effect of temperature on the removal of Pb^{2+} and Cd^{2+} from aqueous solution using caladium bicolor (Wild Cocoyam) biomass in a batch sorption process showed that the most suitable sorption temperature was 40°C with maximum sorption capacities of 49.02mg/g and 52.63m/g for Pb^{2+} and Cd^{2+} ion respectively⁷.

The ambient temperature adsorption of metal cation Zn^{2+} , Cd^{2+} and Pb^{2+} on onion pinus pinaster bark pretreated with acidified formaldehyde solution has been reported. The investigation reveals the influences of the pre-treatment condition and of the pH of the cation solution on the adsorption capacity of the bark. They found that the bark was an excellent adsorbent for the removal of toxic ions from waste water with efficiency compared to commercially available adsorbent. Under optimum conditions, the fractions of dissolved ions adsorbed are 85-95% for Pb^{2+} , 55-85% for Cu^{2+} and 51-57% for Zn^{2+} respectively⁸. Lead is a group IV element in the periodic table and belongs to period six. It has an atomic number of 82 and atomic mass of 207.19g/mol with electronic configuration of $[Xe] 4f^{14} 5d^{10} 6s^2 6p^2$. It exhibits +2 and +4 oxidation states. An ion exchange resin is an insoluble network polymer which carries ionic group. The resin is capable of exchanging its counter ion with other ions of the same charge and may thus be used to exchange its counter ions with other ions present in a surrounding solution.

In practice, resins are produced in the form of small beads of 0.1 - 0.5nm diameter which swell in liquid medium usually water. The amount of swelling in the resin is controlled by the degree of cross-linking⁹. They can be grouped into four general categories; strong acid, weak acid, strong base and weak base. The ion exchange resin can be manufactured into one of the two physical structures; gel or macroporous. Gel resins are homogeneously crosslinked polymers and are the most common resins available. They have exchange sites distributed evenly throughout the beads. The amount of divinyl benzene cross-linking used in the synthesis of a bead determines the relative strength of the bead. Standard strong acid cation resin used for softening, which is the most common ion exchange media is almost always an 8% divinylbenzene cellular material¹⁰

Macroporous resins were introduced commercially in 1959 and are made with large pores that permit access to the interior exchange site. They are also referred to as macroreticular or fixed

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pores resins. Macroporous resins are manufactured by a process that leaves a network or pathways throughout the beads. This sponge like structure allows the active portions of the bead to contain a high level of divinylbenzene cross linking without affecting the exchange kinetics. Unfortunately, it also means that the resin has a lower capacity because the bead contains less exchange sites. The pores can take up to 10 to 30% of the polymer. This reduces the ion exchange capacity proportionately¹⁰. Gel resins usually have higher operating efficiencies and cost less. A macropour gives better physical stability, primarily because of its sponge-like structure. It also eliminates some of the breakage that may occur from osmotic stress. The higher surface area in a macroporous anion resin gives better organic fouling resistance. In a cation resin, the higher cross-linking level gives better oxidation resistance¹⁰.

MATERIALS AND METHODS

The orange mesocarp was air dried for a period of two weeks and milled using a hand grinder. Standard sieve plate was used to obtain 106µm particle size of orange mesocarp and stored in plastic containers until ready for use at ambient atmospheric condition. Ten gramme (10g) of the 106µm size of the orange mesocarp was weighed and poured into a filter paper. This was then placed in the soxhlet extractor. The soxhlet extractor was placed in a round bottom flask containing 500ml of methanol. A reflux condenser was connected to the top of the soxhlet extractor on the thermostatic water bath and supported with a retort stand. The methanol was heated to reflux at 65⁰C while the extraction of the sample was completed when a clear methanol solution was observed in the side arm of the soxhlet extractor. The above procedure was repeated for the remaining 410g sample of the dried orange mesocarp¹¹. The extract was then poured into a beaker and heated for 2 hours to evaporate the remaining methanol in the extract. Same was done for the residue.

PREPARATION OF THE RESIN

About 2.5g of the Orange mesocarp extract and 2 drops of 0.1m NaOH were added to 5.5ml of formaldehyde and 13.0ml 4-hydroxylbenzene sulphonic acid in a 500ml beaker. The mixture was heated at a temperature of 50⁰C on a thermostatic water bath with constant stirring until a hard viscous red colouration was observed. Final polomerization was affected by heating the resin at 60⁰C for 4 hours in an oven. The above procedure was repeated with the orange mesocarp residue sample. The resin synthesized using the orange mesocarp extract was termed O.M.E. while that synthesized from orange mesocarp residue was termed O.M.R.

PREPARATION OF STOCK AND STANDARD SOLUTION

About 1000ppm stock of Pb(II) ion was prepared by dissolving 1.59g of lead nitrate in a standard flask and the volume was made up to 1000ml mark. Serial dilution of the stock solution was carried out to obtain working standards of 5ppm, 10ppm, 15ppm, 20ppm and 25ppm metal ion solution. The absorbance of Pb ion was analysed using an Atomic Absorbance Spectrophotometer.

REACTING THE O.M.R RESINS AND O.M.E RESINS WITH Pb(II) ION SOLUTION .

About 0.5g of the synthesized resin from the orange mesocarp extract and residue was added to 15ml of 5ppm lead (II) ion solution in a conical flask and corked. The mixture in the flask was

shaken vigorously in a mechanical shaker (120 oscillations per minute) for one hour and filtered to obtain a clear filtrate for atomic absorption Spectrophotometric analysis. The above procedure was repeated with the 10ppm, 15ppm, 20ppm and 25ppm Pb (II) ions solution which were carried out at room temperature.

pH TEST

The pH of the different concentration of Pb (II) ion solution was measured before and after the exchange process by a pH paper.

RESULTS AND DISCUSSIONS

About 150g of extract was obtained from 420g of orange mesocarp with residue of about 269g.

$$\text{Percentage yield of O.M.E.} = 150 \times \frac{100}{420} = 35.7\%$$

$$\text{Percentage yield of O.M.R.} = \frac{269}{420} \times 100 = 64\%$$

The resin synthesized from the orange mesocarp extract was observed to be of a gel-type as it was homogeneously cross-linked and the exchange sites were distributed evenly throughout the resin. However, the resin synthesized from the residue was of a macropore type as large pores that permit access to the interior exchange were observed. It was also sponge-like in nature. The results of the atomic absorption spectrophotometric analysis on varying metal ion concentration for the resin synthesized from O.M.E. and that from O.M.R. are presented on table 1 and 2. The percentage metal ion removal for the O.M.E. resins and O.M.R. resins are also shown on these table (1 and 2) respectively. The plots of percentage metal ion removal versus metal ion concentrations for both resins are represented on figure 1. The results indicate higher percentage removal of 84.60% at lower metal ion concentration of 5ppm for O.M.E. resin and 41.00% metal ion removal at lower metal ion concentration of 5ppm for O.M.R. resin. The O.M.E. resin which is a gel type resin performed better at lower concentration because the exchange sites of the resin were evenly distributed on the resin while that of O.M.R. resin which is a macroporous resin performed better at higher concentration due to the large pores that permit access of more ions to the interior exchange sites of the resin.

EFFECT OF METAL ION REMOVAL ON SOLUTION pH

The values of the change in pH before and after metal ion removal are presented on table 3 and 4 for O.M.E. and O.M.R. resins respectively. The results for the O.M.E. resin and the O.M.R. resin shows constant high values for the solutions pH before the ion exchange reaction and constant lower values after the ion exchange reaction. This reveals that the solution pH was affected by metal ion removal.

CONCLUSION

The gel and macroporous resin was compared using the removal of Pb(II) ions from aqueous solution by cation exchange resin synthesized from orange mesocarp. The result indicated that O.M.E. resin exchanged more ions at lower metal ion concentration while the O.M.R. resin exchanged more ions at higher metal ion concentrations. This study justifies that O.M.E. and O.M.R. resins can serve as a good source of purifying polluted water with metal ions.

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TABLES AND FIGURE**Table 1: percentage metal ion removal at varying concentration for O.M.E. resin**

Initial metal ion Concentration (ppm)	concentration at equilibrium (ppm)	percentage metal ion removal (%)
5	0.77	84.60
10	1.68	83.20
15	3.32	77.08
20	5.67	71.65
25	5.59	77.64

Table 2: percentage metal ion removal at varying concentration for O.M.R. resin

Initial metal ion Concentration (ppm)	concentration at equilibrium (ppm)	percentage metal ion removal (%)
5	2.95	41.00
10	6.08	39.20
15	7.45	50.33
20	7.54	62.30
25	5.78	76.88

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Table 3: pH values of various metal ion concentrations for the O.M.E. resin.

Initial metal ion Concentration (ppm)	pH	concentration at equilibrium (ppm)	pH at equilibrium
5	6.8	0.77	1.5
10	6.8	1.68	1.5
15	6.8	3.32	1.5
20	6.8	5.67	1.5
25	6.8	5.59	1.5

Table 4: pH values of various metal ion concentrations for the O.M.R. resin

Initial metal ion Concentration (ppm)	pH	concentration at equilibrium (ppm)	pH at equilibrium
5	6.8	2.95	1.5
10	6.8	6.08	1.5
15	6.8	7.45	1.5
20	6.8	7.54	1.5
25	6.8	5.78	1.5

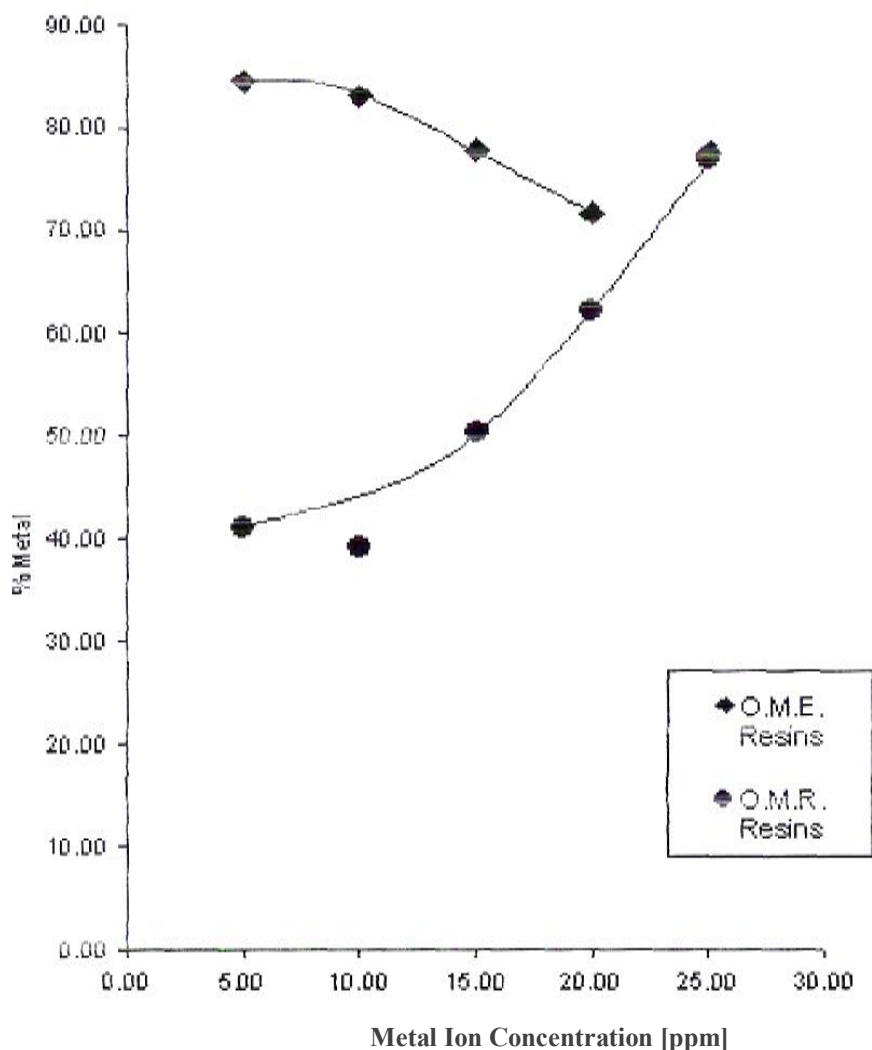


Figure 1: Plot of Percentage Metal ion Removal at Varying Concentrations for the Resins

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