Removal of Cr³⁺ and Mn²⁺ Ions from Aqueous Solution Using Immobilized Bio-Sorbent

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

Original Research Article

ABSTRACT

This research studied the removal of heavy metal ions from aqueous solution using a bio-sorbent. The bio-sorbent was prepared by entrapping or caging *Moringa oleifera* bark (IMOB), within a polymeric matrix of Calcium Alginate to produce immobilized bio-sorbent. The sorption efficiencies of heavy metals (Cr³⁺ and Mn²⁺ ions) were investigated using the IMOB biomass. The result obtained showed that the sorption efficiency of Cr³⁺ and Mn²⁺ by IMOB were 99.22% and 90.13% respectively. The sorption efficiency with respect to contact time, initial metal concentration, ionic strength and pH were investigated. The result obtained showed that the sorption capacity by IMOB decreases with increase in ionic strength, but it increases as the pH, contact time and initial metal concentration increases. The ability of IMOB to adsorb heavy metal ions as shown from the result portrays it as a potential cheaper method for waste water treatment.

Keywords: Immobilization; Moringa oleifera bark; calcium alginate; sorption.

1. INTRODUCTION

Water is one of the abundantly available substances in nature. It is an essential constituent of all living things [1]. Availability of safe water is an essential pre-requisite for sustainable development. Desert is not habitable because of lack of water [2]. Throughout history

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the quality of drinking water has been a factor in determining human welfare. Faecal pollution of drinking water has frequently caused water borne diseases that have negatively affected the human race. Unwholesome water polluted by natural sources has caused great hardship for people forced to drink it or use it for other purposes.

Polluted water contains some toxic materials of various categories. One of the spectacular contaminants is heavy metal, which man exploits to better his life, but indirectly finds its way back to his environment and finally his body. It is well recognized that the presence of metals ions in the environment can be detrimental to a variety of living species [3]. Unlike organic pollutants, metals are non-biodegradable and because of this the removal of heavy metals becomes essential. The heavy metal ions are stable and persistent environmental contaminants since they cannot be degraded and destroyed. These metal ions become harmful to aquatic and other forms of life through the food chain. Water contaminated by toxic metal ions remains a serious public health problem for human health. Although numerous methods exist to remove heavy metal ions from aqueous solutions such as chemical precipitation, ion exchange resins, dialysis, membrane filtration etc., these methods are expensive and hard to come by especially among rural dwellers. Therefore, a cheap and effective method must be sourced if we are to provide potable water for our increasing population [3]. Bio-sorption of heavy metal ions from aqueous solution is relatively a new technology for the treatment of industrial waste water. This method utilized naturally occurring waste material derived from biomasses which are relatively cheap and abundant in nature.

The tree *Moringa oleifera* is one of the abundantly grown plants in northern Nigeria. The tree is grown in semi-arid, tropical and semi-tropical areas. It grows best in dry sandy soil, and it tolerates poor soil, it is also fast growing and drought resistant tree. Among the natives, the seed, and root are used for water treatment, such as removal of clay and other suspended matters [4,5]. Although *M. oliefera* is use for water treatment, the process itself is associated with the problems of the plant part leaching into the clarified water, and development of odour by the treated water with time. Therefore if this plant part is to be utilized for waste water treatment, it must be scientifically prepared in a way as to overcome the present challenges of leaching and odour [6]. This study is aimed at immobilizing *M. oleifera* bark with sodium alginate in order to possibly produce a sorbent for metal ion removal from aqueous solution.

2. MATERIALS AND METHODS

Sodium alginate, calcium chloride, sodium hydroxide, hydrochloric acid were obtained from British Drug House (BDH). *M. oleifera* bark was sampled from Ngurore in Yola South Local Government Area of Adamawa state, Nigeria. All materials were used as supplied.

2.1 Preparation of *Moringa oleifera* Bark

The *M. oleifera* bark was sun-dried. It was then powdered in a mortar and sieved through 100 µm mesh to produce a fine powder. The sieved material was packed in polythene bag for further use.4.0 g of the bark powder was weighed and dissolved in 100 cm^3 of distilled water and left to stand for 12 hours.

2.2 Preparation of Sodium Alginate and Calcium Chloride

Sodium alginate was prepared by weighing 4.0 g of sodium alginate and making it up to 100 cm^3 marks in a volumetric flask with distilled water. It were left overnight for complete dissolution to give 4% w/w. Calcium chloride, 0.12 M, was prepared by weighing 26.28 g into 1L flask and made up to the mark with distilled water [7].

2.3 Immobilization of the *M. oleifera* Bark

50 cm^3 of the dissolved *M. oleifera* bark was thoroughly mixed with 50 cm^3 of 4% stock solution of sodium alginate and stirred vigorously for even mixing in 250 cm^3 beakers. The mixture was subsequently poured into another beaker containing 30 cm^3 of 0.12 M calcium chloride solution. The reaction was allowed retention time of 1 hour for complete precipitation. The precipitated blend solid was then filtered and allowed to dry at room temperature (30ºC). The dried solid mass was stored in a polythene bag for further use. The above process was repeated by mixing different sets of blend with 4% of the stock solution of the sodium alginate and *M. oleifera* bark admixture at a ratio of 100:0, 90:10, 80:20, 70:30, 60:40 and 50:50. The precipitates so obtained were dried and kept separately for further use [7].

2.4 Preparation of Metal Ions Stock Solution as Synthetic Waste Water

The metal ions chosen for this study are Cr^{3+}, and Mn^{2+}. Standard solutions of the metal ions were prepared from their anhydrous salts and serial dilutions was made by dissolving 2.95 and 3.46g of chromium (III) Nitrate and manganese Nitrate, respectively, in distilled water and made up to the 1 L mark in the flask to obtain 1000 ppm of the metal ions. From the stock solution, serial dilution of 200 ppm of each metal ion was prepared in distilled water.

2.5 Sorbent Sorption Capacity

From 200 ppm of each metal ion solution, 50 cm^3 was taken into a conical flask (covered with a rubber bung), 0.2 g of dried sample added and then shaken with a flask shaker for 2 hours. The solution was then filtered and the concentration of the residual metal ion in the filtrate was determined using Atomic Absorption Spectrophotometer AAS (Model 210 VGP, Buck Scientific) [6]. This process was repeated for all metal ions.The final metal ion concentration over the initial metal ion concentration multiplied by 100 gave the sorption capacity in percentage. The work was done in triplicates and average value taken.

2.6 Determination of the Effect of pH on Sorption Efficiency

The sorption characteristics of the *M. oleifera* immobilized bark at different pH values (1.0 to 6.0) were investigated at 30ºC. In this experiment, 1.0 M hydrochloric acid and 1.0 M sodium hydroxide were used to adjust the pH of the solution as the case may be. The residual metal ion was measured as stated above [6].

2.7 Determination of the Effect of Ionic Strength on Sorption Efficiency

The ionic strength of the working solution of 200 ppm was adjusted with 0.1, 0.5, 1, 1.5 and 2.0 g of NaCl to obtain various desired concentrations of 0.1–2.0% w/w respectively. This was followed by the addition of 0.2 g of IMOB sample to 50 cm^3 of the prepared solution and the equilibrium concentration of the residual metal ion was determined.

2.8 Determination of the Effect of the Contact Time on Sorption Efficiency

In order to determine the kinetics of the sorption for the various metal ions, several set of samples consisting of 0.2 g of the dried sorbent and 50 cm^3 of the metal ion solution for each of the ions was prepared. As the samples were undergoing agitation (on the shaker), they were removed one after the other at a predetermined time interval ranging from 0.5 hours to 24 hours for analysis. The solution was filtered and analysed for residual metal ion. This was done for all metal ions at 30ºC.

2.9 Determination of the Effect of the Initial Metal Ion Concentration on Sorption Efficiency

The effect of the initial metal ion concentration on the sorption capacity of different samples consisting of 50 cm^3 each of different metal ion concentrations ranging from 5 ppm – 100 ppm, but each containing 0.2 g of the dried *M. oleifera* bark were prepared and shaken until equilibrium was obtained at 30ºC. The synthetic wastewater was filtered and analysed for residual metal ion concentration.

3. RESULTS AND DISCUSSION

3.1 Sorption Efficiency

Fig. 1 shows the equilibrium sorption capacity of immobilized *M. oleifera* bark. It can be seen that the higher sorption capacity was recorded for Cr^{3+} while the lower value for Mn^{2+}. The values of 99.22, and 90.13% were recorded for Cr^{3+}, and Mn^{2+} respectively. The results from the present study are comparable with those reported from similar studies [7,8].

The differences observed in the sorption capacities for different metal ions can be explained in terms of differences in hydration free energy, the ability of metal to form covalent bond with ligand, the metal polymeric cations within the biomass structure and the nature of the surface sites available [9].

3.2 Effect of pH on Sorption Efficiency

Fig. 2 depicts the effect of pH on the removal of heavy metal ions. The removal efficiency was studied at pH range of 1.0 – 6.0 at 30ºC. It is clear from the figure that as the pH increases; the sorption of heavy metals also increases. This finding is similar to the ones reported by

Osemeahon [10] and Wuyep [7]. The result obtained indicates optima pH value of 5.0 for both Cr^{3+} and Mn^{2+}. The pH optima for metal ions could be probably due to the solution chemistry of the metal ion [11]. The pH is an important parameter as it strongly affects bio-sorption capacity. This is because it affects surface charge of bio-sorbent, ionic mobility, degree of ionization and the speciation of biosorbate species [12,13]. Increasing the pH leads to precipitation of insoluble hydroxide or hydrated oxide, thereby lowering the metal ion availability for sorption. On the other hand, a decrease in pH results in an increase in the hydrogen ion concentration and hence possible competition for bonding sites [14].

3.3 Effect of Ionic Strength on Sorption Efficiency

Another important parameter in bio-sorption is the ionic strength. Sodium is common in many wastewater and high Na^+ concentration leads to high ionic strength which can give rise to a reduction in metal ion uptake [15]. Fig. 3 shows the effect of ionic strength on sorption efficiency of metal ions. It is evident that the sorption efficiency decreases as the ionic strength increases. This is attributed to the difference in the ionic osmotic pressure between the sorbent and the external solution [16].

The difference in osmotic pressure between the sorbent and the external solution increases as the ionic strength of the external solution increases. Therefore, the sorption of metal ions decreases when the ionic strength of external solution increases [17,16]. In addition, the effect of ionic strength can however be explained because of competition of Na^+ with other metal ions for electrostatic binding to the biomass. Since deprotonated free carboxyl, hydroxyl or sulphate groups are negatively charged, they will electrostatically attract any cation [18].
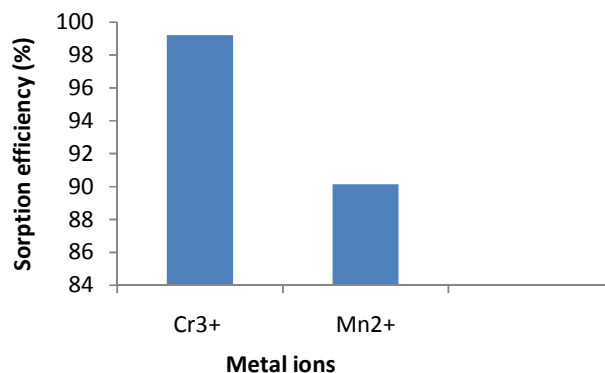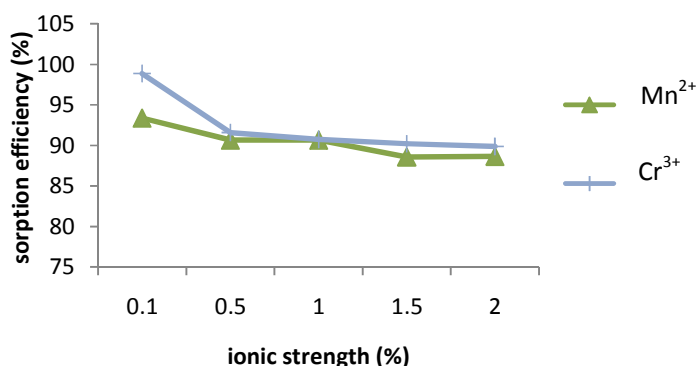

Fig. 1. Sorption efficiency of metal ions by IMOB
Time: 2 hrs, Temperature: 30℃, Initial metal concentration: 200 ppm, pH: 6
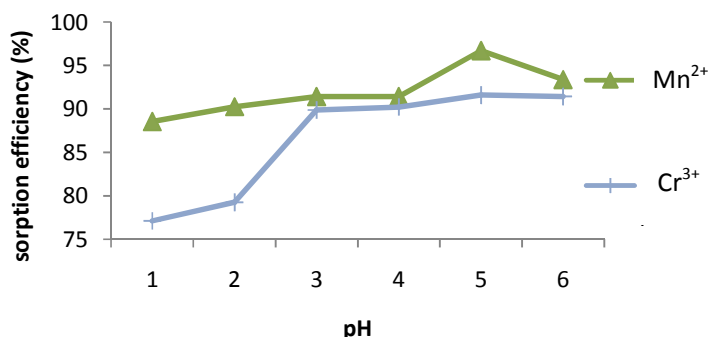
Fig. 2. Effect of pH on sorption efficiency of Cr^{3+} and Mn^{2+} by IMOB
Time: 2 hrs, Temperature: 30℃, Initial metal concentration: 200 ppm

Fig. 3. Effect of ionicstrength on sorption efficiency of Cr^{3+} and Mn^{2+} by IMOB
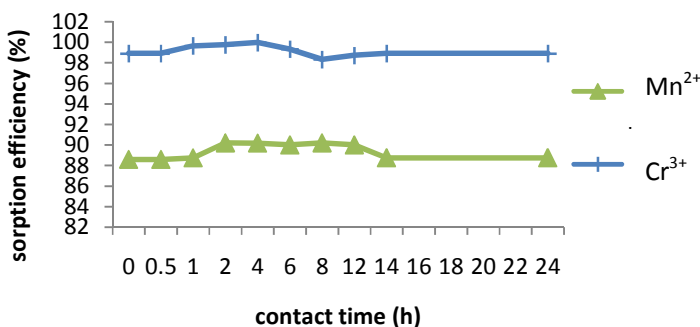*Time: 2 hrs, Temperature: 30ºC, Initial metal concentration: 200 ppm, pH: 6*

3.4 Effect of Contact Time on Sorption Efficiency

The contact time is a key parameter for wastewater treatment. A short contact time to attain the saturation stage and maximum amount of the metal ion sorbed at equilibrium indicate the rapid transport of metal ion from the bulk to the outer and inner surfaces of bio-sorbent. Thus, the period of equilibrium is an important factor by which to judge the feasibility of a bio-sorbent for its use in water quality control as it affects the economic value of the sorbent [19].

Fig. 4 shows the effect of contact time on sorption capacity of heavy metal ions. It can be seen that equilibrium time of 2 hours was recorded for Mn^{2+} and 4 hours recorded for Cr^{3+} ion .The rapid sorption of metal ions can be attributed to the highly porous structure of the bio-sorbent which provides a large surface area for sorption of the metal ions to the binding sites.

3.5 Effect of Initial Concentration on Sorption

The result of metal ions sorption by the immobilized *M. oleifera* bark is shown in Fig. 5. The feasibility and efficiency of a bio-sorption process depends not only on the properties of the bio-sorbent, but also on the metal ion concentration. The initial concentration provides an important driving force to overcome all mass transfer resistance of the metal between aqueous and solid phase [20]. It can be observed that the removal of the metal ions by the sorbent increases with the initial increase in initial metal concentration. This behaviour can be explained in terms of increase in flux of the metal ion. The flux of the metal ion varies directly with the metal ion concentration and hence there should be an increase in flux with increase in initial concentration [21,22,23].

Fig. 4. Effect of contact time on sorption efficiency of Cr^{3+} and Mn^{2+} by IMOB
Temperature: 30ºC, Initial metal concentration: 200 ppm, pH: 6
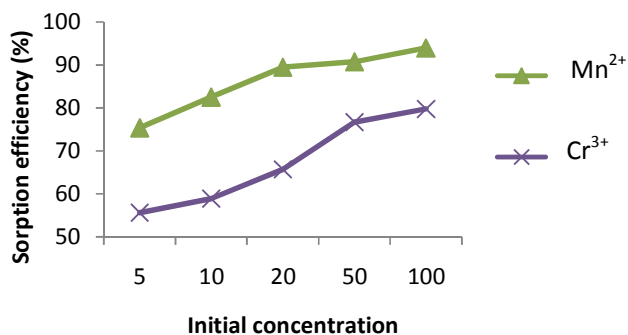
Fig. 5. Effect of initial concentration on sorption efficiency of Cr^{3+} and Mn^{2+} by IMOB
Time: 2 hrs, Temperature: 30ºC, pH: 6

The increase in uptake can also be explained on the basis that at lower initial metal ion concentration, the ratio of the initial mole of the metal ion to the available surface area was low, so sorption becomes independent of the initial concentration. However, at higher concentration, the sites available for sorption becomes less in comparison to the moles of the metal ion present in solution and hence the removal of metal ion is strongly dependent upon the initial solute concentration [19].

4. CONCLUSION

In this research work, the immobilization of *M. oleifera* bark was achieved by caging it within a polymeric matrix with sodium alginate. The sorption capacity of Cr^{3+} and Mn^{2+} was found to be 99.22 and 90.13% respectively. In the same context, the sorption efficiency decreases with an increasing ionic strength, but increases with increase in pH values, initial metal ion concentration and contact time. Based on the result obtained, it can be concluded that IMOB is a potential sorbent for the removal of metal ions from waste water.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Author has declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=902&id=16&aid=8630