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Full Length Research Paper

The removal of heavy metal ions from aqueous solutions using sour sop seeds as biosorbent

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Heavy metals discharged into the environment from various industries constitute one of the major causes of water and soil pollution. Conventional methods for the removal of heavy metals from waste waters are often cost prohibitive. These constraints have caused the search for alternative technologies for metal sequestering to cost-effective environmentally acceptable levels. One of the exploitations is the use of biomaterials. The results obtained after contacting for 120 min showed that sour sop seeds achieved the removal of 77.6, 68.5, 56.4and 40.6% for Cu^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} ions, respectively. The residual metallic ion concentrations were determined using an Atomic Absorption Spectrophotometer (AAS). The ability of sour sop seeds to absorb metal ions as shown from the results can be used for the development of an efficient, clean and cheap technology for effluent treatment.

Key words: Toxic, heavy metal, ions, synthetic, adsorption, biosorption.

INTRODUCTION

Over the past 20 years, a number of legislations have come into force to control pollution. Problems associated with waste water disposal in developing countries and especially in Nigeria can be attributed to lack of adequate treatment/management policies coupled with ineffective legislation on the part of entrusted government agencies (The Environmental Protection Act, 1991). The inadequacy of our conventional methods of river dumping was further exposed by the death of fishes and even deforestation of nearby trees on the shore, affecting also, human and animal lives. Therefore, the study of the existing effluent disposal methods, facilities, and attitudes is essential in order to make a positive impact on our environmental hygiene.

The discharge of metallic ions in industrial effluent is of great concern because their presence and accumulation have a toxic effect on living species (Ko et al, 2000). Industrial wastewater containing metal ions such as nickel, lead, copper, zinc and aluminium are common because their metals are used in a large number of Industries such as electroplating, batteries manufacture, mine, metal finishing, brewery, pharmaceutical, and so on. Heavy metals are toxic to aquatic organisms even at very low concentration. Most of these minerals were present in our environment only in minute amounts until recent centuries, when the orientation toward industrialization and production brought about our many technological advances. But technology, like medicine, has its side effects. At present, these toxic metals have polluted our atmosphere, our waters, our soil, and food chain.

In the discharge of metal ions in industrial effluent using bio-adsorption process has been an area of extensive research because of the presence and accumulation of toxic carcinogenic effect on living species. The most common and harmful heavy metals are aluminum, lead, copper, nickel, chromium and zinc. They are stable elements that cannot be metabolized by the body and get passed up in the food chain to human beings. When waste is disposed into the environment, a further long-term hazard is encountered. There are possibly more problems from these metals, which interfere with normal bodily function, than have been considered in most medical circles. Reviewing all of our vitamins and minerals has shown us that most every substance that is useful can be a toxin or poison, as well. Metals are known primarily and almost exclusively for their potential

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toxicity in the body, though commercially they may have great advantages.

A conventional method for removing metals from industrial effluents includes chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion-exchange and adsorption. Most of these methods suffer with high capital and regeneration costs of the materials (Huang and Wu, 1975). Therefore, there is currently a need for new, innovative and cost effective methods for the removal of toxic substances from wastewaters. Biosorption is an effective and versatile method and can be easily adopted in low cost to remove heavy metals from large amount of industrial wastewaters. Recent studies have shown that heavy metals can be removed using plant materials such an palm pressed fibers and coconut husk (Tan et al., 1993), water fern *Azolla filiculoidis* (Zhao and Duncan, 1997), peat moss (Gosset et al., 1986), duck weed *Wolffia globosa* (Upatham et al., 2002), lignocellulosic substrate extracted from wheat bran (Dupont et al., 2003), *Rhizopus nigricans* (Bai and Abraham, 2001), cork and yohimbe bark wastes (Villaescusa et al., 2000) and leaves of indigenous biomaterials, *Tridax procum-bens* (Freeland et al., 1974). Apart from the plant based material chemical modification of various adsorbents, phenolformaldehyde cationic matrices (Singanan et al., 2006), polyethylonamide modified wood (Swamiappan and Krishnamoorthy,1984), sulphur containing modified silica gels (Freeland et al., 1974) and commercial activated charcoals also employed (Verwilghen et al., 2004).

The sour sop is ovoid in shape, covered with short, soft spines dark green in colour, changing to a pale green when ripe. The pulp of the fruit is white, of a 'woolly' texture and pleasantly acidic. The juice is used to make a delightful ice cream or iced drink. The seeds are then removed from the fruit and dried at room temperature. These are then opened with the inner dried part used for the adsorption process. The sour sop fruit grows as far as the month of March.

The aim of this work is to study the removal of toxic heavy metal ions by sour sop seeds from synthetic waste water and to offer this biosorbent as local replacement for existing commercial adsorbent materials.

MATERIALS AND METHODS

Preparation of sour sop seeds

The soup sop seeds were dried for a period of three days. The sour sop seeds were cleaned with distilled water and dried at room temperature. The seeds were grounded with the grinding mill. The ground sour sop seeds were sieved and were of particle size 0.25 to 0.5 mm. This was to allow for shorter diffusion path, thus allowing the adsorbate (sour sop seeds) to penetrate deeper into the effluent more quickly, resulting in a higher rate of adsorption (Adeyinka et al., 2007).

Preparation of synthetic wastewater

The initial concentration used was 5.00 mg/l for copper, 4.00 mg/l for nickel, 20.00 mg/l for lead and 2.50 mg/l for zinc, and the contacting time was varied from 20 to 120 min.

A stock solution of nickel, lead, copper, zinc and aluminium was prepared in distilled water with nickel (II) sulphate, lead (II) nitrate, zinc (II) sulphate, and copper (II) sulphate. All working solutions of varying concentrations were obtained by diluting the stock solution with distilled water. The pH of the effluent was adjusted to a pH of 5 to prevent hydrolysis. The concentration of metal ions in effluent was analyzed by Atomic Absorption Spectrophotometer. For quality control purpose, the diluted water were digested and analyzed with every sample group to track any possible contamination source. A duplicate analyzed for every sample to track experimental error and show capability of reproducing results (Marshall and Champagne, 1995).

Adsorption experiment

The experiments were carried out in the batch mode for the measurement of adsorption capabilities. The bottles with 500 ml capacity were filled with 50 ml of the synthetic wastewater, and 1 g of sour-sop seeds (grind). The bottles were shaken for a predetermined period at room temperature in a reciprocating shaker for 2 h at 300 rpm. The separation of the adsorbents and solutions was carried out by filtration with whatman filter paper No. 42 and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual metallic ion concentrations were also determined using an Atomic Absorption Spectrophotometer (AAS).

RESULTS AND DISCUSSION

Effect of time on removal of metal ions

Figure 1 showed the percentage removal of the various metal ions by the sour sop seeds adsorbent. For all the metal ions present in the synthetic wastewater, there was a progression in the percentage removal of metal ions present in the synthetic wastewater with time. From the result of the adsorption experiment Cu^{2+} ions had the highest percent removal of 77.6 at the end of 120 min, followed by Ni^{2+} ions, Zn^{2+} ions and Pb^{2+} ions with 68.5, 56.4 and 40.6, respectively.

For sour-sop seeds, there was a progression in the rate of adsorption but it was not linear at any time. Also, from Figure 1, it was observed that with increase in time, the adsorption rate of the sour sop seeds increased. It was also observed that the rate of adsorption increased significantly for some of the metal ions present in the synthetic wastewater between 60 – 80 min of contact time. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

Effect of dosage on removal of metal ions

Figure 2 showed that the adsorbent dose of 1.0 g there was an increase in the adsorption rate. The larger the surface area, the larger the amount of metal ion adsorbed. This appears to be due to the increase in the available binding sites in the biomass for the complexation of the heavy metals (Gong et al., 2005). This would

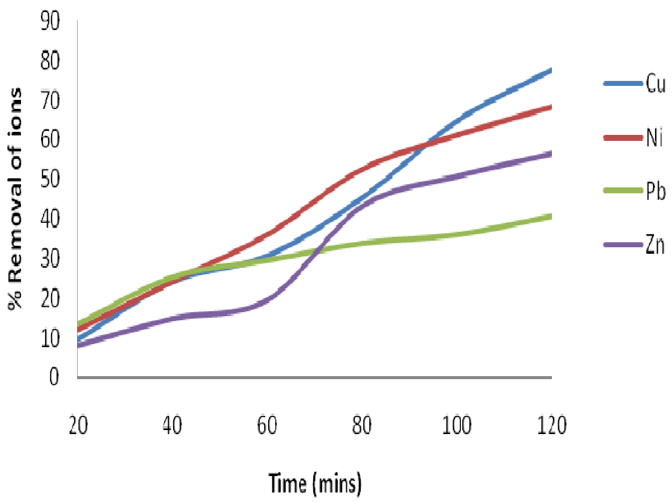

Figure 1. Removal of heavy metal ions from aqueous solutions (50 ml, pH 5) with time using sour sop seeds (1 g) as biosorbent. The initial concentration used was 5.00 mg/l for copper, 4.00 mg/l for nickel, 20.00 mg/l for lead and 2.50 mg/l for zinc, and the contacting time was varied from 20 to 120 min.

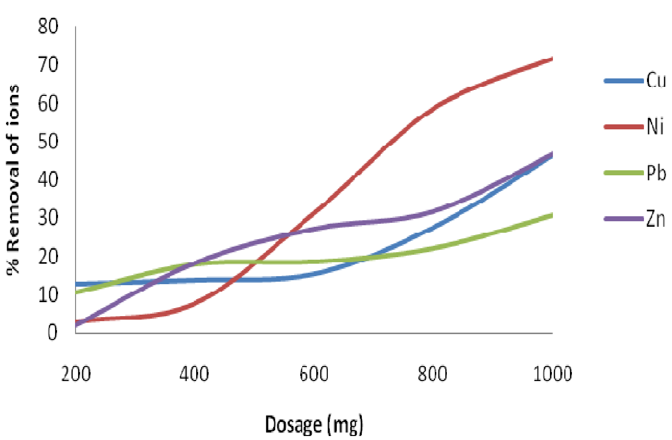

Figure 2. Removal of heavy metal ions from aqueous solutions (50 ml, pH 5) with increasing dosage of the heavy metals using sour sop seeds (1 g) as biosorbent for 2 h.

probably explain the high percent removal of the heavy metals. The sour-sop seeds were able to achieve the percent removal of 71.5, 46.6, 46.4, and 30.8 for Ni^{2+}, Zn^{2+}, Cu^{2+} and Pb^{2+} ions, respectively.

Effect of pH on removal of metal ions

Figure 3 showed that sour-sop seeds had a decrease in the adsorption rate for Cu^{2+} and Zn^{2+} ions and an increase in the adsorption rate for Pb^{2+} and Ni^{2+} ions when the pH of the synthetic waste water was between the value of 5 and 7. When alkalinity increased that is from pH value of 7 to 9 there was a further decrease in the

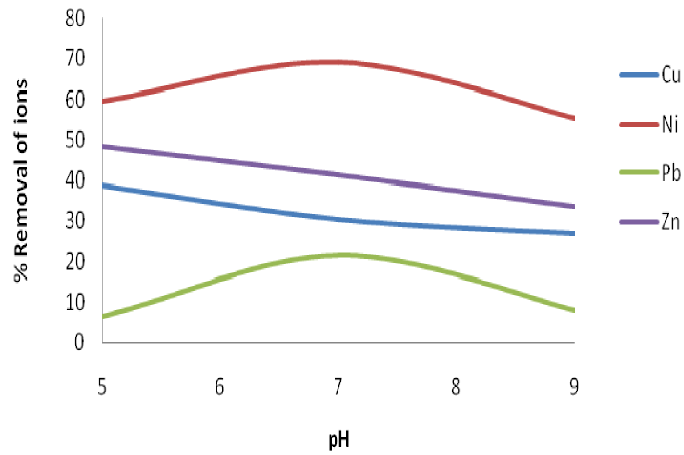

Figure 3. Removal of heavy metal ions from aqueous solutions (50 ml) at different pH using sour sop seeds as biosorbent for 2 h. The initial concentration used was 5.00 mg/l for copper, 4.00 mg/l for nickel, 20.00 mg/l for lead and 2.50 mg/l for zinc

rate of adsorption by sour-sop seeds for Cu^{2+}, Zn^{2+}, Pb^{2+} and Ni^{2+} ions in the synthetic waste water. Results obtained from the adsorption experiment it can be seen that the highest rate of adsorption by sour-sop seeds was 69.0% removal for Ni ions in the synthetic waste water at pH value of 7.

With increase in pH from 5 to 9, the degree of protonation of the adsorbent functional group decreased gradually and hence removal was decreased. A close relationship between the surface basis of the adsorbents and the anions is evident. This is similar to the findings of others, where the interaction between oxygen-free Lewis basic sites and the free electrons of the anions, as well as the electrostatic interactions between the anions and the protonated sites of the adsorbent are the main adsorption mechanism (Leon et al., 1992; Radovic et al., 1997; Faria et al., 2004).

Conclusion

The removal of metal ions in synthetic wastewater by using biosorption technology was studied. Based on the results, the following conclusions can be drawn. The grinded sour sop seeds were very effective in removal of Ni^{2+} ions from the synthetic waste water. Sour-sop seeds are efficient biomaterial for removal of some heavy metals from industrial wastewater. The percent removal of Ni^{2+} ions was 71.5 with an effective dose of 1.0 g of bioadsorbent (sour-sop seeds). This process can be effectively used in the heavy metals removal in industrial wastewater.

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