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FULL LENGTH ARTICLE

Waste Water Treatment Using Shells of Marine Source

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ABSTRACT
Bio-adsorption is a promising technology for the removal of heavy metals, fluorides, reactive textile dyes, and organic toxicants and also precious metals from industrial effluents, all of which have hazardous effects on the aquatic system, and which, through the process of biomagnifications, have resulted in adverse health effects in human beings. The aim of this work is to ascertain the potential of raw materials available in nature as redundant and excess such as Bivalve shells, Oyster shells and Crab shells with a few modifications, in the removal of heavy metals like Mercury, Cadmium, Arsenic, Lead, Nickel, and also fluorides and dyes, thus enabling these new and improved bio-adsorbents to have a greater efficiency. The raw materials selected for the experiment has shown good sorption capacities in adsorption of metals, each with an initial concentration of 100 ppm, which was seen to have reduced by greater than 98%-99%. Life cycle assessment of the raw materials has revealed that the beds can function with the same efficiency even after a passage of ten bed volumes indicating that the same beds can be reused several times before reaching saturation limits. This manner of water treatment is highly economic with no sludge generation unlike other techniques and these adsorbents, being biological, are easy to dispose of without concerns of degradation. This is a clean and green technology where there is an almost insignificant amount of energy consumption at the initial stage for the preparation of bio-adsorbents from raw materials; apart from this, the entire process is passive. The water obtained after purification can be used for various domestic and agricultural purposes, and with further treatment steps, can be of potable quality.
Keywords: *Bio-adsorption; Waste water; Heavy metals; Shells*

INTRODUCTION

Water resources are of paramount importance to all ecological communities as well as for the human up–growth. However, with the onset of the industrial revolution and with the increase in technological development, anthropic activities have resulted in the notable increase of toxic pollutants in the environment. According to a report compiled by the World Economic Forum in collaboration with, to name a few, Oxford University, University of Pennsylvania, and National University of Singapore, water crisis ranks 3rd in the Global Risks 2014. Water bodies, being one of the prime resources, when contaminated with toxious pollutants like heavy metals, organic toxicants, reactive textile dyes, and fluorides, disrupt and destroy the fragile ecology which humans have been trying to build for centuries.

Indiscriminate discharge of contaminants such as arsenic, mercury, lead, nickel, cadmium and so on, have resulted in its accumulation in the aquatic biota leading to its biomagnification. This subsequently causes severe health hazards in humans and other living organisms.

METHODOLOGY

1. Collection of Raw Materials

Materials required for studies such as Bivalve shells, Oyster shells and Crab shells were collected.

2. Preparation of Bio-adsorbents:

The collected three types of shells were washed clean using water and dried in sun for about 8-10 hours. 100gms each type of shells were crushed separately using mortar and pestle to form small pieces and then it was finely powered using mixer.

The bivalve shell powder (BP), oyster shell powder (OP), and crab shell powder (CP) were sieved using fine sieves and stored separately.

3. Preparation of dye solutions, metal solutions:

3.1 Dye solutions:

0.1gm of various dyes such as Acid red dye, vat blue dye , reaction dye pink, orange dye were weighed in 100 ml of distilled water to prepare dye solutions.

The optical maxima of all the dyes were determined by using colorimeter.

3.2 Metal solutions:

100 ml of various metal stock solutions, namely, Lead, Mercury, Nickel, cadmium and arsenic were prepared at a concentration of 100ppm each. All solutions were prepared in double distilled water.

4. Preparation of columns

Weighed quantities of BP, OP and CP were used to make the beds of the columns. Three sets of columns were prepared for all experiments in order to compare the efficiencies between BP, OP and CP for every toxicant under investigation. Initial studies were conducted using 10 ml syringes which were packed with adsorbent beds up to 8 ml, leaving the remainder 2 ml of syringe for toxicant solutions to be added.

Further studies were conducted using 25 ml chromatography columns where a constant weight of BP, OP and CP were required to obtain a bed of height approximately 10 cm in their separate column.

The packed beds were then subjected to water wash 2-3 times to ensure all residual substances were eluted in order to eliminate any background interference. When the water had been completely drained from the columns, the beds were ready for bio-adsorption.

All the tests were carried out in syringes or columns to identify the adsorption capacity of the prepared beds in a small scale. This greatly reduced the volume of the effluents, the chemicals, and the raw materials required for the study as well as the time. These results were then used to select the adsorbents and parameters that served best in the aim to remove toxicants on an industrial scale.

5. Acid Digestion of Adsorbent Materials

The BP, OP and CP were subjected, individually, to conc. Sulfuric acid digestion in order to check whether the adsorbents possessed additional property of adsorption. 15g of each type of powders were mixed separately in 10 ml acid. These mixtures were allowed to cool for 1 hour and then water washed 2-3 times to neutralize it. The column beds were prepared by these acid treated adsorbents for adsorption of metals.

6. Base Digestion of Adsorbents Materials

The BP, OP, and CP were subjected, individually, to base digestion by mixing 15g of each type of powders in 10% of 250ml NaOH solution. These mixtures were kept for 1 hour and then water washed 2-3 times to neutralize it. The column beds were prepared by these base treated adsorbents for adsorption of metals.

7. Life cycle assessment of adsorbents

One of primary areas of focus in our study was to assess the life span of each of the adsorbents packed in columns in order to analyze the number of times a particular quantity of adsorbent can be utilized before it gets saturated. For convenience, for every toxicant, a total of 10 cycles were conducted (10 bed volumes added) for each of the columns having desired amount of adsorbents. This was done for all metals (100ppm). All the samples from all the trials were prepared for AAS analysis.

8. Spectrophotometric determination of fluoride

Spectrophotometric methods are widely used in the determination of fluoride because of advantages such as simplicity, convenience, accuracy and reproducibility . They are based on the reaction of fluoride with coloured metal chelate complexes, producing either a mixed-ligand ternary complex or replacement of the ligand by fluoride to give a colourless metal-fluoride complex and the free ligand with a colour different to the metal-ligand complex. malachite green carbinol base provided by Aldrich, and aluminium chloride hexahydrate provided by Fluka were used without any further purification. Solutions were prepared using double-distilled water. Malachite green ligand solutions and their aluminium complex solutions were prepared using ethanol from Merck (96%). Standard fluoride stock solution was prepared by dissolving 100 g of sodium fluoride provided by Merck in 100 ml water. The complex solutions for the spectrophotometric measurements were prepared as 1:2 ratios from aluminium and ligand of 1×10^{-4} M in ethanol solutions, and the solutions were then diluted to the concentration ($\approx 5 \times 10^{-5}$ M) suitable for the spectrophotometric measurements.

Reaction of fluoride with the prepared complex solutions

Various amounts of fluoride were added in the range 0–2 $mg \cdot \ell^{-1}$ to a 10mℓ test tube containing aluminium complex solution of chrome malachite green in ethanol (5×10^{-5} M, to make up 2.5 ml).The absorbance was measured at the wavelengths of maximum difference (622 nm for malachite green) in the electronic spectra between the ligand and the complex. The spectra for the reaction of different amounts of fluoride with the complex were compared by taking 1ml of filtrate after adsorption by column beds.

RESULTS AND DISCUSSIONS

Table 1: Results of adsorption of acid red dye by shells

MATERIALS	**Absorption of acid red dye** (at 520 nm)	
	Initial OD (Before adsorption)	**Final OD** (After adsorption)
BP	1.82	0.20
OP	1.82	0.17
CP	1.82	0.03

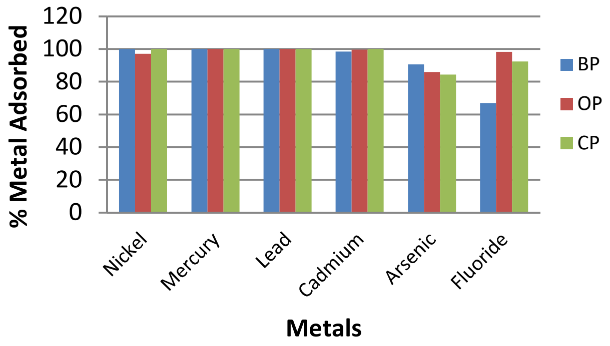

Fig 1: Adsorption Capacity of Metals by Adsorbents

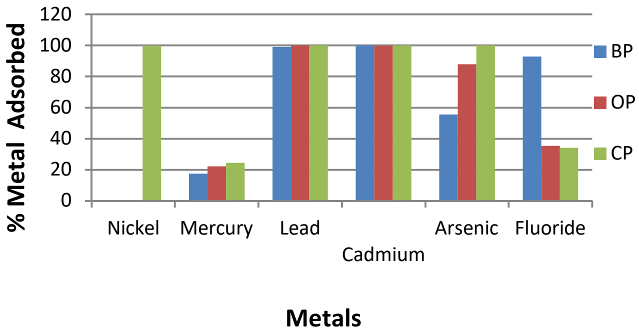

Fig 2 : Adsorption Capacity of Metals by Asdorbents on Acid Digestion

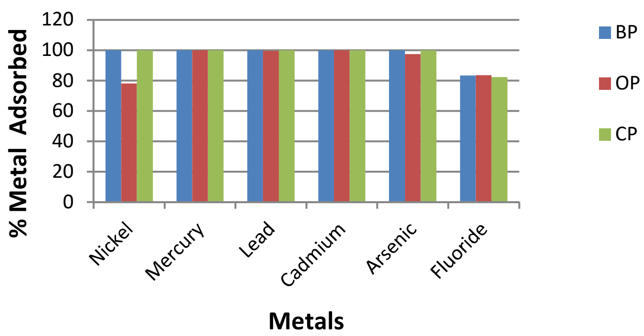

Fig 3:Adsorption Capacity of Metals by Asdorbents on Base Digestion

Life Cycle Assessment of Adsorbents:

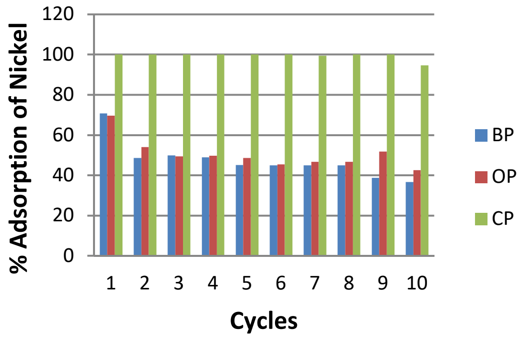

Fig 4: Life Cycle Assessment of Nickel

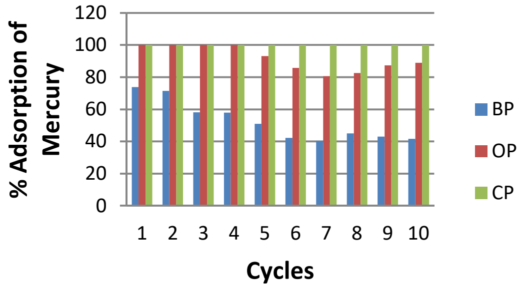

Fig 5: Life Cycle Assessment of Mercury

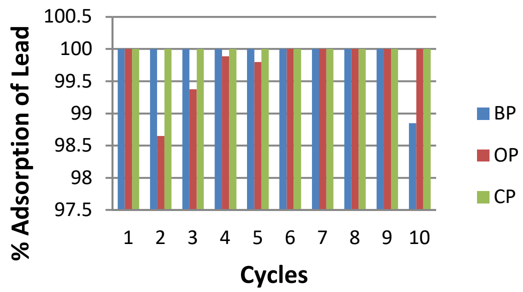

Fig 6: Life Cycle Assessment of Lead

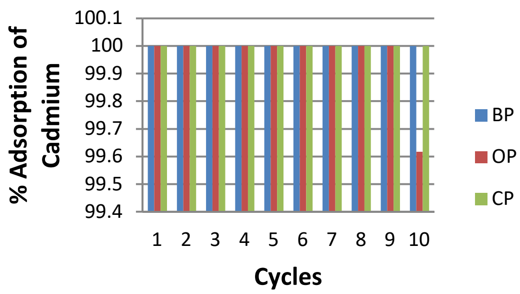

Fig 7: Life Cycle Assessment of Cadmium

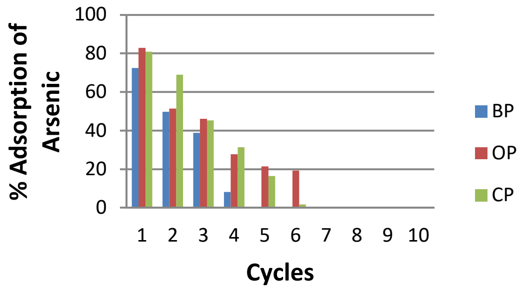

Fig 8: Life Cycle Assessment of Arsenic

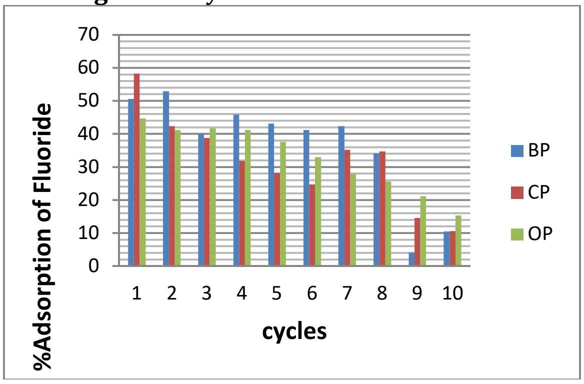

Fig 9: Life Cycle Assessment of Fluoride

CONCLUSION

CP showed an overall better adsorption efficiency compared to BP and OP. It showed 100% removal for all metals under study except for Arsenic which it showed 85% removal. In the life cycle assessment of adsorbents CP showed 100% efficiency in adsorption of metals even after passing 10 bed volumes of metal solutions. CP as a bio-adsorbent showed no saturation even after 10 passes which could only mean that CP had not yet reached saturation and have high productivity in metal removal that it requires much higher concentrations of toxicants to reach a saturation point . This indicates that the beds can be reused several more times before facing the need for regeneration. BP and OP showed 98% to 99% removal for all metals except arsenic for which BP showed 91% removal and OP showed 85% removal. In life cycle assessment BP and OP showed 100% removal for Cadmium and Lead for all 10 cycles. They showed 50% saturation for Nickel and Mercury for 10^{th} cycle. Arsenic showed 100% saturation for the 5^{th} cycle itself.

The adsorption of metals followed the trend: Mercury> Lead> Nickel> Fluoride> Cadmium> Arsenic. Mercury and Lead removal was found to be 100% followed by Lead which showed 99% removal. Nickel and Cadmium showed almost 98%-99% removal for all materials tested. This manner of water treatment is highly economic with no sludge generation unlike other techniques and these adsorbents, being biological, are easy to dispose of without concerns of degradation. This is a clean and green technology where there is an almost insignificant amount of energy consumption at the initial stage for the preparation of bio-adsorbents from raw materials; apart from this, the entire process is passive. The water obtained after purification can be used for various domestic and agricultural purposes, and with further treatment steps, can be of potable quality

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