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BIOSORPTION OF HEAVY METALS USING CRAB SHELL IN AQUEOUS MEDIUM

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ABSTRACT

The biosorption of some heavy metals found in effluents of a boat manufacturing company and oil waste water of two oil exploration companies in Brass and Port Harcourt terminals were carried out using crab shell of particle size 0.25-0.8mm. The concentration (mg/l) of the heavy metals found in the effluents were analyzed using Atomic Absorption Spectrophotometer, model 6650. The result of the analysis showed that the boat manufacturing company effluent discharged to the nearby river had 0.711 Pb, 0.012 Cd, 0.068 Cu while that of the oil waste water were 2.07 Pb, 0.044 Cd, 0.286 Cu, 0.904 Cr, 0.112 Ni and 0.026 Co. After biosorption, the Concentration levels of all the heavy metals decreased except Co; the values were: <0.05 Pb, < 0.002 Cd, < 0.01 Cu, for boat manufacturing effluent and < 0.112 Pb, <0.002 Cd <0.017 Cu, <0.04 Cr, <0.02 Ni and <0.03 Co for the oil waste water. Consequently, crab shell which constitutes part of the waste materials in the Niger Delta region is found to be useful as biosorption substance for a number of industrial effluents containing heavy metals which daily endangers the water bodies of the region.

Keyword: Crab Shell, Heavy Metals, Effluents, Biosorption.

INTRODUCTION

Biosorption is the passive, non-metabolically mediated process of metal binding to living or dead biomass (Rangsayatorn *et al,* 2002). It is simply defined as the binding and concentration of heavy metals from aqueous solutions (even very dilute ones) – by certain types of inactive, dead, microbial biomass. Some types of biomass are waste by-products of large – scale industrial fermentations and sea weeds (Volesky, 1986) these types of biomass can accumulate in excess of 25% of their dry weight in deposited heavy metals such as Pb, Cd, U, Cu, Zn, Cr and others. In biosorption, metallic species sometimes could be deposited in the solid biosorbent through various sorption processes, such as ion exchange, complexation, chelation, microprecipitation etc.

According to Rich and Cherry (1987), the commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, time coagulation, ion exchange, reverse osmosis and solvent extraction. The common disadvantages of these methods include incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal (Ahalya *et al,* 2003). However, the major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimisation of chemical and biological sludge, no additional nutrient requirement regeneration of biosorbent and possibility of metal recovery.

The studies of Ahalya *et al* (2003), has shown that biosorption process involves a solid phase (sorbent or biosorbent: biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases.

The most frequently studied biosorbents are bacteria, fungi and algae (Ilhan *et al,* 2004), Kar and Misra, 2004, Lu *et al,* 2006, Garcia *et al,* 2005, Elfantz and Tel-or, 2002).

Knorr (1991) has reported that both living and dead cell are able to uptake metal ions and offer potential inexpensive alternative to conventional absorbents. The report further observed that living cells are subject to toxic effect of the heavy metal thus resulting to cell death; furthermore, living cells often require the addition of nutrients thereby increasing the Biological Oxygen Demand and Chemical Oxygen Demand in the effluent. These obvious short comings have encouraged more research interest in the use of non-living biomaterials or dead cells as metal binding substance. According to Mofa (1995), dead cells require less care, maintenance and are cheaper.

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The use of agricultural by-products such as Saw dust, rice bran, cotton hulls, orange peels as sorbent have been reported (Bailey *et al,* 1999, Oliveria et al, 2005). Senthilkumarr *et al,* (2000) have shown that fruit juice industrial waste can be utilized in removing toxic heavy metals such as Hg, Pb, Cd, Cu, Zn and Ni from waste waters. The ability of Chitinous material to remove both anionic or cationic contaminants including Cu, Co, Pb and sulphate has been demonstrated by Nui and Volesky (2003). More studies have reported the use of raw Chitinous materials (from crustaceans) for the removal of metal (Rae and Gibbs, 2003). The Chemical group that would attract and sequester the metals in crab shell is acetamido group of Chitin. The greatest demand for metal sequestration today is due to the need to immobilize the metals released to the environment through human technological activities. Studies have shown that dissolved metals (particular heavy metals) escaping into the environment pose a serious health hazard. They accumulate in living tissues throughout the food chain which is a major threat to man's health (Echem, 2010). Senthil and Parthiban (2011) has reported the use of crab shell particles (0.456-0.767mm) to remove Zn^{2+} ions from aqueous solution. They observed that the influence of temperature on metal uptake showed that sorption process is fovourable at room temperature. Their findings showed that crab shell particles exhibited Zn^{2+} ions uptake of 43.83mg/gm. Sudhir et al (2008) investigated sorption potential of pretreated crab shell biomass for Pb^{2+} and Cu^{2+} from aqueous media. At equilibrium, the maximum uptake by crab shell biomass was 19.83 ± 0.29 and 38.62 ± 1.27mg/g for Pb^{2+} and Cu^{2+} respectively. The research findings of Vijayaraghavan *et al* (2006) on the biosorption capacities of crab shell for Cu^{2+} and Co^{2+} were studied at different particle sizes (0.456 – 1.11mm). At optimum particle size (0.767mm), crab shell recorded maximum Cu^{2+} and Co^{2+} uptakes of 243.9 and 322.6mg/g, respectively. The study of the application of biosorption system with acid-washed crab shells for the removal of Ni^{2+} from electroplating industrial effluents had been carried out (Vijayaraghavan *et al,* 2005). The crab shell exhibited uptakes of 15.08 and 20.04mg Ni/g from two types of effluents. The result showed that the use of crab shell in the treatment of nickel-bearing electroplating industrial effluents is viable. The purpose of the present study was to utilize the shell of crab in the removal of Cr, Ni, Co, Pb, Cd and Cu from Oil Waste Water and boat manufacturing company effluents.

MATERIALS AND METHODS

The materials used for this research include: Industrial effluents, measuring cylinder, weighing balance, pH meter, filter paper, conical flask, test tubes, beakers, grinder, oven, sieve, AAS, distilled water and crab shell. The reagent used was $HN0_3$.

Sample Collection and Analysis

Two industrial effluents samples usually discharged to the river were collected; two were from an oil exploration company terminal in Port Harcourt and Bayelsa (Sample A) while the other from a boat manufacturing company site in Port Harcourt (Sample B). The pH of sample A and B were 8.54 and 9.67 respectively. The collected samples were refrigerated at 4^oC prior to analysis. Some crab shells were collected, washed thoroughly with distilled water and dried in an oven at 105^oC for 1 hour. The dried cold crab shells were grinded and sieved to obtain a particle size of 0.25 - 0.80mm.

The effluent samples were brought out of the refrigerator and allowed to standard for 30 minutes under room temperature. 50ml each of the samples were measured into a test tube and acidified with 0.10ml of concentrated $HN0_3$ before aspirating into the Shimadzu atomic absorption spectrophotometer for the determination of the heavy metals of interest: Cr, Ni, Co, Pb, Cd, and Cu for samples.

Another 50ml of each sample was acidified, poured into two separate volumetric flask each containing 2g of the sieved crab shell. The flask was corked, shaken for 2 minutes and allowed to stand for 10 minutes. The solutions were filtered through Whatman No.1 filter paper.

The concentration level (mg/l) of the heavy metals Pb, Cd, Cu, Cr, Ni, and Co) were determined using atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

The results obtained are shown on the table below:

Table I: Levels of heavy metals (mg/l) in effluent sample (A) from Oil exploration company terminals

	Cr	Ni	Co	Pb	Cd	Cu
Before Biosorption	0.904	0.112	0.026	2.07	0.044	0.286
After Biosorption	<0.04	<0.02	<0.03	<0.112	<0.002	<0.017
Tolerable limit	0.10	3.00	-	0.10	2.00	3.00

Table II: Levels of heavy metals (mg/l) in effluent sample (B) from boat manufacturing company in Port Harcourt.

	Pb	Cd	Cu
Before Biosorption	0.711	0.012	0.068
After Biosorption	<0.05	<0.002	<0.01
Tolerable limit	0.10	2.00	3.00

Table III: pH of effluents

Sample	pH
Oil Waste Water	8.54
Boat manufacturing water	9.67
Tolerable limit	5.50 – 9.00

Tolerable Limit Source: Central Pollution Control Board, CPCB, Ministry of Environment and Forests, (1998).

DISCUSSION

The adverse impact of untreated effluents from some manufacturing processes on the environment has been studied (Macaskie and Dean, 1984; Malone, 1989; Nakajina and Sakaguchi, 1986). The outcome of the study and high cost of the commercially available absorbents make it imperative for more investigation on the capability of crab shell to remove heavy metals from industrial effluents.

The levels of heavy metals (mg/l) in oil waste water effluents before biosorption were Cr: 0.904; Ni: 0.112; Co: 0.026; Pb: 207; Cd: 0.044 and Cu: 0.286. After, biosorption the concentration level of the heavy metals of the treated effluent reduced to Cr: <0.04, Ni: <0.02, Co: <0.026; Pb: <0.112; Cd: <0.002 and Cu: <0.017. The heavy metals investigated from boat manufacturing company effluent in Port Harcourt were Pb, Cd and Cu. The concentration levels were Pb: 0.711, Cd: 0.012 and Cu: 0.068 before biosorption and Pb: <0.05; Cd: <0.002 and Cu: <0.01 after biosorption. From these results, the amount of heavy metals uptake by the crab shell from the oil waste water were approximately: Cr: 0.900 (99.58%); Ni: 0.110 (98.21%); Pb: 1.958 (94.59%); Cd: 0.42 (95.45%) and Cu: 0.269 (94.06%); while the uptake from the boat manufacturing company effluent were Pb: 661 (92.97%), Cd: 0.01 (83.33%) and Cu: 0.058 (85.29%).

The pH of the Oil Waste Water and that of boat manufacturing effluent were 8.54 and 9.67 respectively. The pH for the two effluents were basic, which implies that the chitinous material in the untreated crab shell used for this study is anionic hence its ability to remove cations from the media. This finding agrees with the report of Nui and Volesky (2003). Also, Rae and Gibbs (2003) studies confirmed the usefulness of raw or untreated crab shell as biosorbent for heavy metals.

The percentage uptake of heavy metals by the raw crab shell in Oil Waste Water which has a relative lower PH value of 8.54 compared to the boat manufacturing effluent for Pb, Cd and Cu is higher. The results suggest that the degree of alkalinity of the sorbent affects the efficiency of the heavy metal uptake. There was no uptake of Co.

CONCLUSION

The findings of our research agree with report of Hoshi *et al* (1977); the report established the fact that chitin can act as a cation exchanger in basic medium. This high adsorption capacity was ascribable primarily to its remarkable hydrophilicity in cooperation with the relatively high amino group content (Gyliene *et al,* 2002).

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