Adsorption Capacities of Modified Substrates in Bioremediation of Toxic Water Pollutants

Omotoso Toyin, Oluwasegun O Aluko

Abstract— **This paper unveils the potency of bioremediation as a cost effective and environmental friendly method of soil and ground water pollution remediation. A review of conventional methods was carried out in order to evaluate various success of bioremediation in its ability to alleviate toxicity in water and soil. The paper further presents the results and findings of an experimental research on the adsorption of some toxic metals (found in an industrial central sewage treatment site) onto EDTA modified bagasse, coconut fiber and groundnut shell. The trend of the sorption capacity was found to be Fe>Mg>Cu>Cr for bagasse, Fe>Cr>Cu>Mg for groundnut shell and Fe>Cu>Cr>Mg for coconut fiber. Generally, the results show that the EDTA modified bargese possesses the highest adsorption capacity among the substrates for the elements cadmium, and chromium, copper and silver.**

Index Terms— **Modified Substrates, Toxic pollutants.**

I. Introduction

Bioremediation is an ecologically sound and state-of-art technique that employs natural biological processes to remove, especially, toxic and hazardous pollutants from contaminated soil and water bodies. Bioremediation has a long tradition [1] It is documented [2] that biotechnology using microorganisms was invented in an experimental adventure by George .M. Robinson, a petroleum engineer for Santa Maria California, in the 1960's. Till date, the potentials of other materials have increasingly been under research with astonishing successes in the processes listed in table I and other processes described elsewhere.

Table 1: Phytoremediation Processes and Mechanisms of Contaminants Removal.

No	Process	Mechanism	Contaminants
1	Rhizofiltration	Rhizosphere	Organic/ inorganic
2	Phytostabilisation	Complexation	Inorganic
3	Phytoextraction	Hyper-accumulation	Inorganic
4	Phytovolitilization	Volatilization by leaves	Organic/ inorganic
5	Phytotransformation	Degradation in plant	Organics

Heavy metals are conventionally defined as naturally occurring elements with metallic properties (ductility, conductivity, stability as cations) having a high atomic weight and a density at least 5 times greater than that of water and it is toxic or poisonous at low concentrations [3] The most common heavy metal contaminants are: cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) and zinc (Zn). Metals are natural component in soil. Contamination, however, has resulted from industrial activities such as mining and smelting of metalliferous ores, electroplating, gas exhaust, energy and fuel production, fertilizer and pesticide application, and generation of municipal waste [4]. There occurrence and distribution in the environment is as a result of man anthropogenic activities occasioned by his intervention on his environment. Their route classifies them as systemic toxicant and cumulative poison to the organs and system of biotas.

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II. Remediation Technologies

Several brilliant works have been documented on the effective use of fungi as biosorbent of dyes of methyl [5]. The use of white rot fungi is the most unique technology of bioremediation as their ability to degrade structurally diverse xenobiotic organo-pollutants [6], treatment of colored and metallic effluent [7]. Several fungal species have developed a high resistance to heavy metals and developed variety of mechanisms to remove ions form more stable complex. The fungus penicillium has often been found to effectively remove phenantherene in soil [8].

Plants have been used to breakdown, or degrade organic pollutants or curtail and stabilize metal contaminants by acting as filters or traps [9] and metals accumulators (phytoaccumulation) [10, 11] by the processes of phytoextraction [12] which is emerging as the cost effective alternative. These are associated with several issues and constraints [13]. Processes associated with Phytoremediation are listed in the table I below [14] (Ghosh and Singh, 2005). The accumulation of some other heavy metals and trace-elements in many species of wetland plants has also been demonstrated [15, 16, 17 and18]. Water hyacinth has been successfully used in waste water treatment systems to improve the quality of water by reducing the levels of organic and inorganic nutrients [19, 20]. Furthermore, the quality of trace elements that can be accumulated by water hyacinth has been shown to correlate well with concentration of heavy metals in the water [21]. In Taiwan, the suitability of this plant for phytoextracting toxic heavy metals (Cd, Cu, Pb, Ni and Zn) commonly found in municipal wastewater was determined. The concentrations of Cu, Cd Ni, Pb and Zn were analyzed using an ultrasonic nebulizer. The minimum detection found to be 1.3, 1.2, 2.4, 3.2 and 1.3gg/kg respectively. Water hyacinth absorbed heavy metals mostly from the roots and translocates only 6 to 25% to the shoots. Therefore, only the bioconcentration factor in plant root was considered to evaluate the effectiveness of water hyacinth as a phytoremediator.

[22] described biosorption as the passive removal of toxic heavy metals or the–sequestration of the metals by binding them to the cell wall or other ligands. This requires that the

substrate displays high metal uptake and selectivity as well as suitable mechanical properties for applied remediation scenarios.

Adsorption of pollutants from industrial effluents using conventional adsorbents such as activated carbon has been frequently employed. The use of expensive materials makes the processes non cost effective. Various organic fibers of agricultural wastes have been used in the remediation of heavy toxic metals in wastewaters. These include maize cob and husk [23] coconut fiber and sawdust [24 ,25] sunflower stalls [26] Sago waste [27]; cassava waste [28]; peanut skin [29]; medicago sativa (Alfalfa) [30; sphagnum moss peat [31] and many others.

In this paper, the adsorption of heavy metals (cadmium, chromium, copper and silver) from industrial effluent using modified bargese and coconut fiber are determined. These substrates constitute cellulose and lignin with functional group of carboxyl, hydroxyl and amine understood and known to enhance binding of metallic ions and biosorbents [32]

III. Materials and Methods

The biomass underwent a pre-treatment which consists of repeated washing with distilled water until elimination of impurities, drying in an oven for 48 hours, then crushing and sifting to obtain an easily storable powder of granulometric 0.85mm. All chemicals used in the treatment processes in this study were of analytical grade.

Bargese and coconut fiber were activated with 2% (v/v) nitric acid overnight. The activated substrates were modified using Ethylene diamine-tetra acetic acid (EDTA). 30g of each of the activated sample were hydrolyzed with 500ml of 7% (v/v) aqueous nitric acid for l8hrs at 65°C. 17g of the hydrolyzed products (Bargese and coconut fiber) were refluxed in a mixture of 300m1 of pyridine and 56.7g of EDTA for 3h at 70 °C. The mixtures were allowed to cool. 300m1 of deionized water was added and mixtures filtered. The EDTA modified products were washed copiously with deionized water and dried at 50°c for 12hours.

2g of the samples (bargese and coconut fiber) were put into 100ml solution of the metal ions separately and mechanically stirred at a constant speed of 150 rpm at 30 °C for contacts periods of 60mins at 10mins intervals. The pH was adjusted (using a pH-meter Orion Research, Model SA520, USA) to 7.5 for each contact time range by adding 0.1M NaOH. The significance of this addition is to enhance the formation of metal hydroxide solid to be formed and precipitate from the solution. It is important to note here that the concentration of the metals in solution are ensured at a minimum of 0.001mg/L and pH range greater than 7.0 to accommodate the disparity in the metal concentration at different pH.

The samples were filtered rapidly by suction at the end of each contact time (i.e. 10, 20 …and 60 mins).The wastewater was digested in order to bring all the metals in the effluent into soluble forms and make their subsequent extraction to be available for atomic absorption spectrophotometer (AAS) determination. The AAS model Solaar 969, ATI Unicam Comp equipped with a digital direct concentration read out and an air–acetylene burner using single element hollow cathode lamps (ATI Unicam Comp.). When the concentrations were under the detection limit of flame, the AAS external standards in diluted acid were used to calibrate the accuracy of atomic absorption.

Wet digestion of the waste was carried out using mixtures of HNO_3 and H_2SO_4 in the ratio 3:1. 50ml of the effluent was mixed with 15rnl of the digestion mixture; the mixture was then heated until there was an escape of white fumes from the boiling mixture which signifies a complete digestion. The hot digest was cooled and filtered and diluted to 100rnl. The significance of the addition of these chemicals in respect of chromium compound, for example, is to first convert the hexavalent chromium to trivalent chromium in an acidic condition thus enhancing its precipitation.

The filtered digest was used for metals adsorption determination and the values determined as follows:-

Metal in effluent (mg/L) = (Conc. /50rn1)* 1000 of sample

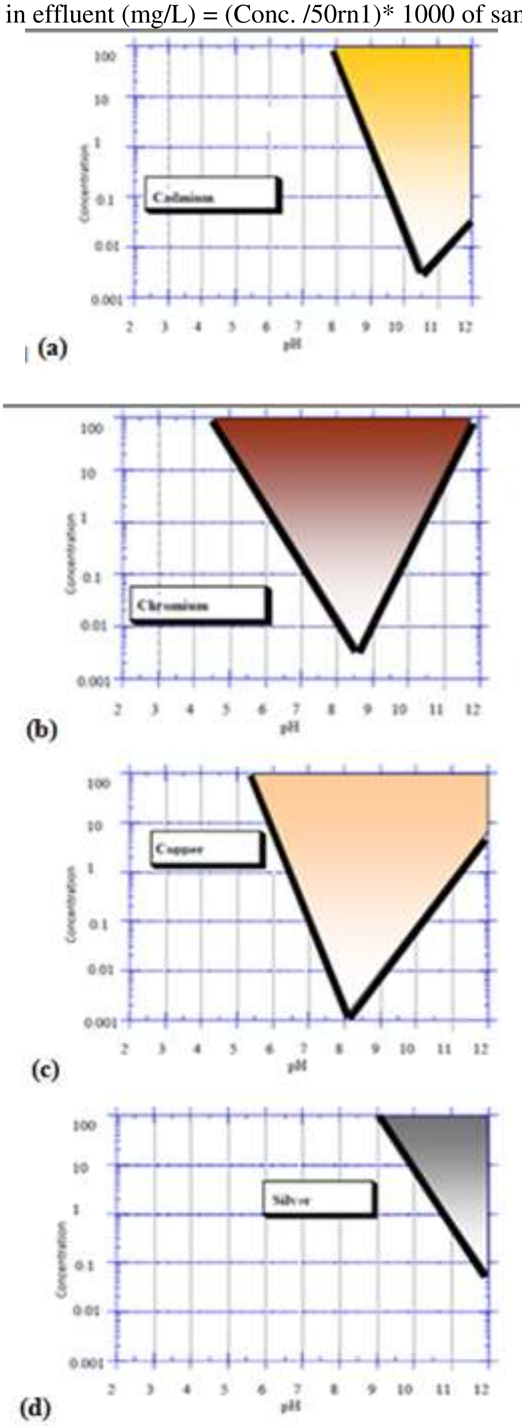

Figure 1: Theoretical solubility of (a) Cadmium hydroxide, (b) Chromium hydroxide, (c) Copper hydroxide and (d) Silver hydroxide

(Extract [32] Ayres, D M. et al 1994): the concentration of metal within the shaded portion signifies precipitation of the metal hydroxide and the region outside illustrates where the metals are dissolved in solution and no removal takes place.

IV. RESULTS AND DISCUSSION

The chemical analysis of the effluent was conducted for the presence of trace metals: the result content of the predominant fraction of the products of the municipal wastes in which four, cadmium, chromium, copper and silver were isolated for determination. The average concentration values of samples were Cd 6.65µg/L, Cr 150µg/L, Cu 215.75µg/L and Ag (µg/L). The pH value of the effluent sample was recorded as 6.5 which is considered to be largely due to bioavailability of the decomposition of other organic deleterious materials. The presence of these metals portends a great danger for the health of the people if such is allowed to leach, untreated, into both surface and ground water which are the major sources of water use for the people especially in a situation where greater percentage of the population are vulnerable.

Bargese adsorbed more of magnesium than any of the substrates but generally, the trend of uptake for bagasse is in the order of Cd > C r > Cu > Ag. Adsorption of mg to bagasse was found to increase with time and decrease with time in Groundnut shell and coconut fiber. Bargese is a good absorbent of Cd, C r, Cu and Ag. The trend of uptake for groundnut shell is in the order of Fe> Cr >Cu >Mg. The trend of uptake for coconut fiber is in the order of Cd > C r > Cu > Ag.

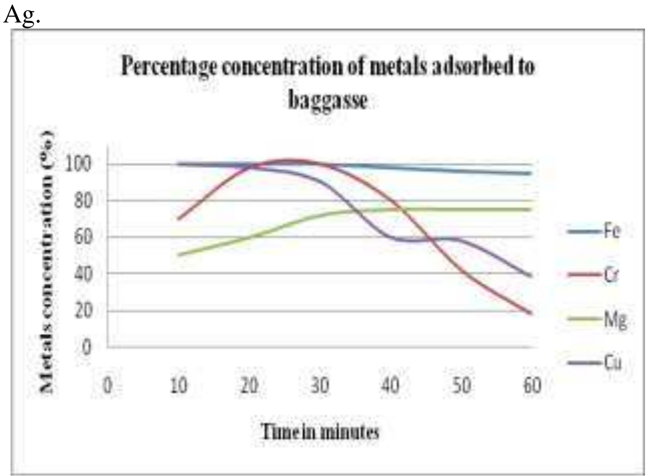

Figure 1: Percentage concentration of metals adsorbed to baggasse

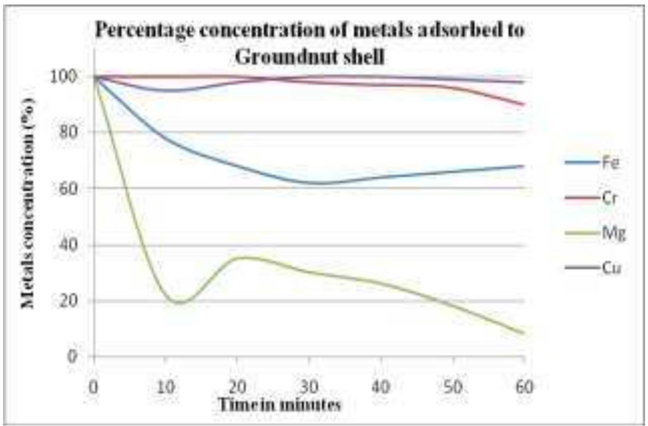

Figure 2: Percentage concentration of metals adsorbed to Groundnut Shell

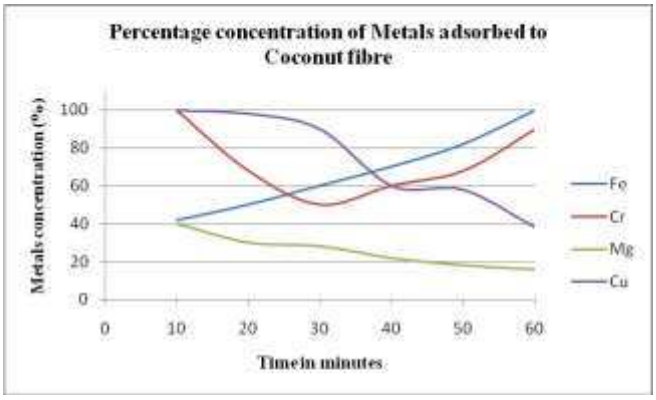

Figure 3: Percentage concentration of metals adsorbed to Coconut Fibre

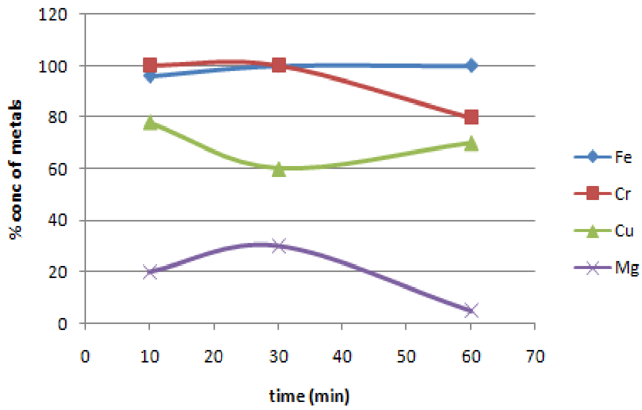

Figure 4: Metals adsorption time Series

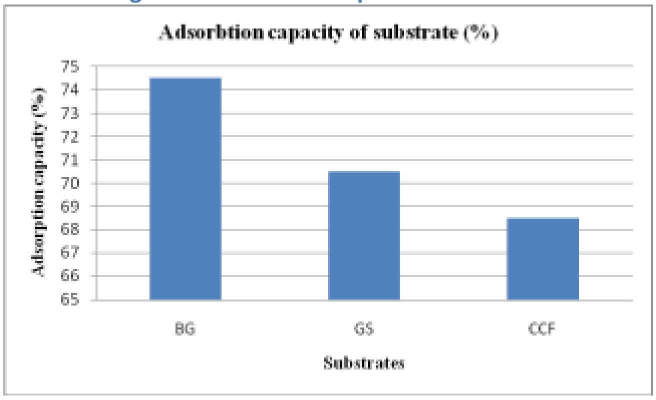

Figure 5 Relative adsorption capacity of the Substrate

It is assumed here that the substrates which are averagely adsorbed the largest quantity of metals generally possesses the highest adsorption capacity, express in percentage. This is presented in figure 4 above.

V. CONCLUSION AND RECOMMENDATIONS

This paper has shown that plant-based technology for removing and detoxifying toxic trace elements from industrial effluent and contaminated water is effective and can be more improved substantially using engineering approaches. Bagasse and coconut fiber which are agricultural wastes have been applied in the partial treatment of toxic wastewater which is a major problem to civil engineers in the remediation of water pollution problems. Also the result of this experiment can be used as a parameter to reduce the weakening effect some of those toxic metals have on water and/or effluent carrying pipes. Since some metals in water reduces the compressive strength of concrete, the removal or reduction of these metals using cheap absorbents such as the ones used in this study and /or more agricultural by-products that are yet to be unveiled will reduce the cost of constriction in toxic areas. With this technique, there is a need for research aimed at fundamental understanding of the parameters involved for result optimization, economies and sustainability of clean environment.

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