

*Short Communication*

# Efficient Extraction of Heavy Metals from Contaminated Water Using Thioglycolic Acid-Modified Oil-Palm Fiber

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Various kinds of agro and wood based fibres can be used to filter both trace and heavy metals from contaminated solutions. The efficacy of thioglycolic acid treated oil-palm fibre was investigated in this study. The result showed maximum absorptions (at pH = 6) of 83.6, 75.6 and 50.8% for Fe<sup>++</sup>, Zn<sup>++</sup> and Mg<sup>++</sup> respectively in the Southern Point (SP) samples. Similarly, 79.1, 78.3 and 77.5% for Fe<sup>++</sup>, Zn<sup>++</sup> and Mg<sup>++</sup> were obtained for Northern Point (NP) samples. The removal efficiency of the metals was pH as well as ionic size dependent. The uptake capacities showed that iron had a higher capacity than zinc while magnesium had the least. This study therefore suggests that thioglycolic acid modified oil-palm fibre is highly efficient in sorption of metals from solutions and should be used as such at a slightly acidic pH.

**Key words:** Heavy metal removal, thioglycolic acid modified oil-palm fibre.

## INTRODUCTION

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increase flux of metallic substances into the aquatic environment. The metals are of special concern because of their persistence. Industrial wastes constitute the major source of the various kinds of metals pollution in natural waters (Horsfall et al., 2003).

In recent years, several studies have been carried out on the removal of toxic metals from the aqueous effluents using agricultural by-products. The use of agricultural by-products in bioremediation of metal ions is an aspect of biotechnology. This is recognized as an emerging technique for the depollution of metals polluted streams and rivers (Volesky and Holan, 1995). The bio-sorption offers an alternative to the remediation of industrial effluents as well as recovery of metals contained in other media (Igwe et al., 2005).

As a result of the expensive nature of the removal / recovery methods of precipitation and ion exchange, which require the use of chemicals and synthetic resins.

Many agricultural by-products that are available at little or no cost have provided a window of opportunities. These agro-based materials have been reported to be capable of adsorbing and removing large amount of metal ions from aqueous solutions (Okieimen et al., 1988).

Several researchers have shown that agricultural waste materials can bind substantial amount of metal ions. These materials include polymerized corn cob (Odozi et al., 1985), modified groundnut husk (Okieimen, 1988), modified peanut shells (Marshall et al., 2001) and cas-sava waste biomass (Horsfall et al., 2003). In this study, the efficacy of thioglycolic acid modified oil-palm fibre was investigated.

## EXPERIMENTAL PROCEDURE

The metal laden water samples were obtained from polluted rivers in Eket Southern and Nsit Atai Northern part of Akwa Ibom State labelled SP and NP respectively. The oil-palm fibre was also obtained from the same location. It was deoiled by stirring in hot deionized water and detergent for 24 h. It was then rinsed in hot deionized water and dried in air for 48 h. The dried oil-palm fibre was ground using electric blender. The fibre was then screened through a set of sieves (250, 150 and 106 µm). The fibre that passed through the 106 µm was used for adsorption studies.

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**Table 1.** Showing percentage of metals adsorbed by thioglycolic acid modified oil-palm fibre.

| Sample | Initial pH | Fe <sup>++</sup> (%) | Mg <sup>++</sup> (%) | Zn <sup>++</sup> (%) | Final pH |
|--------|------------|----------------------|----------------------|----------------------|----------|
| NP     | 2          | 12.4                 | 33.6                 | 40.0                 | 1.7      |
| NP     | 6          | 79.1                 | 77.5                 | 78.3                 | 5.2      |
| NP     | 8          | 69.2                 | 50.5                 | 61.1                 | 7.3      |
| SP     | 2          | 15.0                 | 12.4                 | 20.6                 | 1.9      |
| SP     | 6          | 83.6                 | 50.8                 | 75.6                 | 5.3      |
| SP     | 8          | 37.4                 | 41.3                 | 46.0                 | 7.5      |

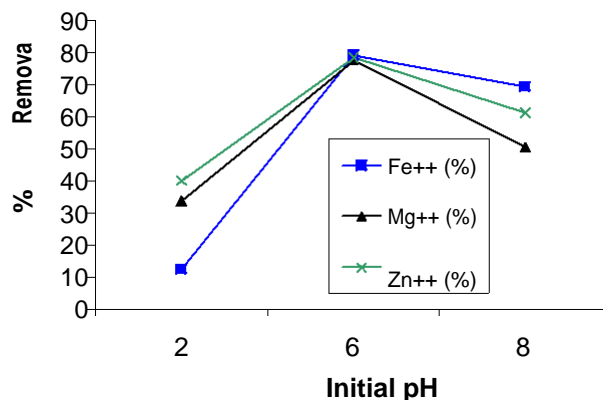
\*NP (Samples from Nsit Atai Northern part) SP (Samples from Eket Southern part)

After this treatment, 500g of the sieved fibre was treated with 1.0 M thioglycolic acid (HSCH<sub>2</sub>COOH) for 30 min and left to stand for 24 h at 28°C. The treated fibre was then filtered using a Whatman No. 41 filter paper. The resulting residue was rinsed with deionized water and allowed to dry. Then 1g of the dried thioglycolic acid treated fibre was measured into 50 ml of the metals polluted samples at different pH of 2, 6 and 8 respectively, shaken and kept for an hour, after which it was filtered and the filtrate analyzed for residual metals using Atomic Absorption Spectrophotometer (AAS unicam model).

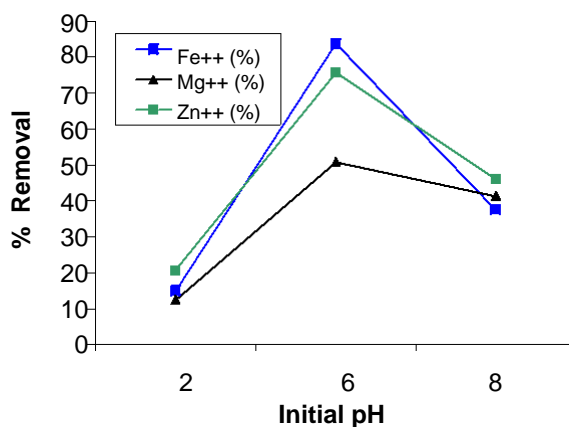
## RESULTS AND DISCUSSIONS

From the result presented, the percentage of Fe<sup>++</sup>, Mg<sup>++</sup> and Zn<sup>++</sup> removed first increased from pH = 2 to pH = 6 and then declined at pH = 8. The highest removal rate of 83.6% was recorded for Fe<sup>++</sup> at pH = 6 in SP sample. This was followed by 79.1% for Fe<sup>++</sup> at the same pH for the NP sample. The least efficiency of removal was recorded at pH = 2 while at pH = 8, there was a drop in the percentage of adsorption for all metals (Table 1).

The removal of metals from aqueous solutions by adsorption is related to the pH of the solution, since pH affects the surface charge of the adsorbents degree of ionization. The influence of pH on the adsorption of the metal ions was highest at pH = 6 for all the metals (Figures 1 and 2). In all cases, there were reductions in the initial pH after sorption. This is generally believed to be due to exchange of hydrogen atoms in the substrate by metal ions (Okieimen et al., 1988). It is thought that the presence of a relatively high concentration of H<sup>+</sup> in the medium would influence this exchange from the sub-strate since decreasing solution pH increases H<sup>+</sup> concentration in the solution, which will coordinate with OH<sup>-</sup> groups to form OH<sub>2</sub><sup>+</sup> and thereby reduce the number of negative sites on the adsorbent and therefore cause the repulsion of metal ions (Ofomaja et al., 2005). On the other hand, increasing pH reduces the amount of H<sup>+</sup> in solution and promotes ionization of <sup>-</sup>OH groups. It can be seen (Figures 1 and 2) that the removal of Fe<sup>++</sup>, Mg<sup>++</sup> allophane, smectite and similar clays, the characteristic



**Figure 1.** A plot of initial pH VS % removal in NP



**Figure 2.** Plot of initial pH VS % removal in SP.

variable charge on the lattice with varying pH causes an increase of cation retention with increasing pH. The highest rate of removal for SP and NP was recorded for Fe<sup>++</sup> at pH = 6 which incidentally had the heaviest load. Similar observation was noted by Ofomaja et al. (2005).

More so, the uptake capacities of thioglycolic acid treated oil-palm fibre showed that Fe<sup>++</sup> had a higher capacity than Zn<sup>++</sup> while Mg<sup>++</sup> had the least. This differential sorption of different ions may be attributed to the differences in their ionic sizes. The smaller the ionic size, the greater its affinity to reactive sites (Horsfall Jnr. et al., 2003). The percentage adsorption of Zn<sup>++</sup> > Fe<sup>++</sup> > Mg<sup>++</sup> could be linked to their ionic radii of 0.69 < 0.74 < 0.78 Å for Zn<sup>++</sup>, Fe<sup>++</sup> and Mg<sup>++</sup> respectively. This trend was also observed for Cu<sup>++</sup> and Zn<sup>++</sup> with other biological adsorbents (Braukmann, 1990). A decrease from maximum adsorption was noticed at pH = 8 due to hydrolysis resulting from increase in pH. According to Huhcey (1983), metals and Zn<sup>++</sup> increased from pH = 2 to pH = 6 and then declined at pH = 8. Arpa et al. (2000) pointed out that in all have the ability to be hydrolyzed because of higher charge size.

A number of studies have been carried out on metal removal by biosorption, all of which showed considerable reduction, for instance 60 – 80% removal using agricultural by-product (Abia et al., 2002), greater efficiency of about 74 – 100% lead and 77.2% Cadmium removal was recorded using tea waste (Mahvi et al., 2005). Similar result of 71.3% removal was recorded for zinc (Adeyiga et al., 2005). It is imperative to note that lignocellulosic materials when used, apart from their sorption activities are biodegradable since most lignocellulosic materials especially agricultural fibres will degrade in contact with moisture.

## Conclusion

Pollution of the aquatic environment with toxic valuable metals is widespread. Consideration of the modes of purifying these contaminations must be given to strategies that are designed to high thorough put methods while keeping cost at minimum. Biosorption readily provides an efficient alternative to traditional physiochemical means for removing toxic metals. We have investigated the effectiveness of thioglycolic acid modified oil-palm fibre in the removal of  $Fe^{++}$ ,  $Zn^{++}$  and  $Mg^{++}$  from polluted rivers in Akwa Ibom State, Niger Delta, Nigeria. The result obtained was pH dependent and is quite promising in terms of numerical strength of the percentage removal for the above priority metal investigated

## REFERENCES

- Abia AA, Hosfall M (Jnr.), Didi O (2002). Studies on the Use of Agricultural by products for the Removal of Trace Metals from Aqueous Solution. *J. Appl. Sci. Environ. Manage.* 6: 89-95
- Adeyiga AA, Hu L, Grear T (2005). Removal of Metals Ions from Wastewater with Natural Wastes Retrieved on 22/8/05 from <http://www.netl.doc.gov/publications/proceedings/98/98hbcu/liang-v.pdf>.
- Arpa C, Say R, Satiroglu N, Bekstas S, Yurum Y, Geric O (2000). Heavy metal removal from aquatic systems by Northern Anatolian Smectites. *Turk. J. Chem.* 24: 209–215.
- Braukmann BM (1990). Industrial Solutions Amenable to Biosorption. In Voksky B. (ed). *Biosorption of Heavy Metals*, CRC Press Florida, USA pp. 52 – 63
- Horsfall M (Jnr.), Abia AA, Spiff AI (2003). Removal of Cu(II) and Zn(II) ions from wastewater by cassava (*Manihot esculenta* Ganz) Waste Biomass. *Afr. J. Biotechnol.* 2 (10): 360–364.
- Huhcey JE. (1993). *Inorganic chemistry*. 3rd Ed. Harper International S. J. Edition Publishers, London pp. 67–112.
- Igwe JC, Ogunewe DN, Abia AA (2005). Competitive adsorption of Zn (II), Cd (II) and Pb (II) ions from aqueous and non-aqueous solution by maize cob and husk. *Afr. J. Biotechnol.* 4 (10): 1113 – 1116
- Mahvi AH, Naghipour D, Vaezi F, Nazmara S (2005). Teawaste as an Adsorbent for Heavy Metal Removal from Industrial Wastewaters. *Am. J. Appl. Sci.* 2(1): 372 – 375.
- Marshall WE, Seo CW, Chamarthy S (2001). Adsorption of selected toxic metals by modified peanut shell. *J. Chem. Tech. Biotech. b:* 113–118.
- Odozi TO, Okeke S, Lartey RB (1985). Studies on Binding of Metals Ions with Polymerized corn cob and a composite Resin with sawdust and onion skin. *Agric. Waste.* 12: 13–21.
- Ofomaja EA, Unabonah IE, Oladoja NA (2005). Removal of lead from Aqueous solution by palm kernel fibre. *S. Afr. J. Chem.* 58: 127–130
- Okieimen FE, Maya AO, Oriakhi CO (1988). Sorption of Cadmium, Lead and Zinc Ions on sulphur containing chemically modified cellulosic materials. *Int. J. Environ Anal. Chem.* 32: 23–27.
- Volesky B, Holan ZR (1995). *Biosorption of Heavy Metals*. *Biotechnol. Prog.* 11:235-250.