

THERMODYNAMIC ASSESSMENT OF ANIONIC LIGANDS - MODIFIED PALM KERNEL FIBRE IN THE SORPTION OF SOME TOXIC METALS

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ABSTRACT

Coconut husk and palm kernel fibre are separately pulverized to obtain 250µm particle size and then blended in a 1:1 ratio to obtain the Blended Palm Kernel Fibre (BPKF). The BPKF was thiolated and then employed as adsorbent in adsorption studies of Co^{2+} , Cd^{2+} and Ni^{2+} ions. The effects of pH and anionic ligands (EDTA, Cl^- and ethylenediamine) on the sorption process are also investigated. The results indicate that for the ligand – free adsorbent, sorption generally increased with increase in pH, optimum pH being established between 5.0 and 6.0 for the three toxic metal ions studied. The presence of the ligands (ethylenediaminetetraacetic acid, EDTA, ethylenediamine, en, and chloride ion, Cl^-) generally improved the sorption capacity for the adsorbent, the best being Cl^- at optimum pH of 2.0 (for Co^{2+}) and 5.0 (for Ni^{2+} and Cd^{2+}). The thermodynamic studies reveal that the adsorption process is non – spontaneous in the forward direction.

KEYWORDS: Toxic metals, sorption, blended palm kernel fibre (BPKF)

INTRODUCTION

Toxic metal pollution in surface and underground waters has become a problem we must solve or face uncertain future (Jackson and Jackson, 1997; Manahan, 1994; Miroslav and Vladimir 1999).

Since natural means can no longer cleanse the aquatic environment of the enormous quantities of the toxic metals generated continuously, some workers have devised diverse means hoping to achieve this. Expectedly, treatment at source is the only practical means of controlling toxic metals pollution (Miroslav and Vladimir, 1999). Waste waters containing toxic metals may be treated by adding anions that can cause precipitation of the offending metals as insoluble salts (Jackson and Jackson, 1997). Other methods include membrane filtration, carbon adsorption and co-precipitation/adsorption (Smith, 1973). The past few decades have witnessed an increasing use of agricultural wastes to remove some toxic metals from water, based mainly on adsorption phenomenon (Jideonwo et al, 2007; Okolo and Okuo 2004).

This work is a veritable contribution to the search for cheap and effective materials and methods to remove toxic metals from contaminated water. Blended Palm Kernel Fibre (BPKF) fortified with strong anionic ligands was employed in the study for possible applications in isolating some toxic metal ions (Co^{2+} , Cd^{2+} and Ni^{2+}) from certain industrial wastewaters. This serves the twin purposes of avoiding littering the environment with waste palm kernel and coconut fibres, as well as gainfully employing same to detoxify some wastewaters. This method is cheap and affordable. Reduction in the cost of industrial – effluent treatment by devising cheap and affordable alternatives is highly desirable.

MATERIALS AND METHOD

Sample Preparation

Samples of coconut and palm fruit were obtained from Uselu Market, Benin City, Nigeria. The palm fruit was treated with hot water and mashed to separate the palm kernel fibre. The palm kernel fibre was then treated with warm water and petroleum ether until the oil was completely removed. The coconut husk was mechanically pulled off from the pericarp of the coconut. The oil free fibre and the coconut husk were oven dried at a temperature of 80°C. Both materials were milled using a thoroughly washed mortar and local grinding mill and sieved with 250µm mesh size sieve. The blending procedure of Okuo and Okolo (2006), was adopted to obtain the blend of the two biomass.

Thiolation of the Blend

About 50.0g of the blend sample as hydrolyzed with 7% w/v H_2SO_4 for about 2h, filtered and the residue washed with distilled water and air dried. The dried residue was treated with 0.10M thioglycolic acid solution for 26h in a well ventilated laboratory to ensure the complete thiolation of the blend. The thiolated sample was then filtered and the residue thoroughly washed with distilled water and ethanol to aid the de – acidification process. Finally, the thiolated residue was air dried and used for the adsorption experiment.

Sorption Process

In order to determine the equilibrium concentration and the amount of metal ions removed, 10.0ml of 50.0ppm Co^{2+} ion solution was prepared in five different flasks with pH of 2, 3, 4, 5, and 6. The pH of the metal solutions was adjusted with 2.0M ethanoic

acid and 0.1M sodium hydroxide solutions. The effect of anionic ligands – ethylenediaminetetraacetic acid (EDTA), ethylenediamine (en) and chloride ion (Cl^-) was studied separately. Each ligand (0.01M) was placed in each of the flasks containing the metal ion solution. About 0.5g of the blended sample was then added to the metal ion solution in the flasks and shaken with a mechanical shaker for 1h. Filtration was done after an equilibration period of 75min. The blank (ligand free metal solution), Ni^{2+} and Cd^{2+} ions solutions were also treated in the same manner. The concentrations of the metal ions sorbed were determined with atomic absorption spectrophotometer. The Cl^- ion solution was prepared from analar grade sodium chloride salt. The NaCl, EDTA and en reagents were of BDH analar grade.

RESULTS AND DISCUSSION

The effect of anionic ligands on the removal of metal ions from aqueous solution is shown in Table 1. Generally the presence of the ligands enhances the adsorption capacity of the substrate (BPKF). It might be that in aqueous solution, the absence of the ligands provides the proton free access to the adsorption sites on the substrate, thereby limiting the amount of the toxic metal ions that can possibly be adsorbed. On the other hand, the ligands (when present) bond with most of the protons, thereby preserving the adsorptive sites on the substrate which can then be used in adsorbing the toxic metal ions. Co^{2+} ion appeared to be more favoured in the adsorption experiment. This might be attributed to the small ionic size/radius of cobalt ion. The ionic radii of the three ions – Co^{2+} , Ni^{2+} and Cd^{2+} are respectively

0.65, 0.69 and 0.95Å (Lee, 1999). Smaller ions usually complex best and are stable. In an aqueous medium, Co^{2+} ion is easily hydrated in the presence of the three ions forming complexes such as $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (Lee, 1999). This enhances the sequestration of the Co^{2+} ion by the adsorbent more than the other metal ions. The hydration of these metal ions follows the order: $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$ and this is in agreement with the order of adsorption in this study.

It was also observed in this study that adsorption increases with increasing pH for the ligand – free metal solution. This observation may be attributed to protonation (at lower pH) of the functional groups present in the substrate giving it a positively charged ion. This brings about repulsion between the adsorbent and positively charged ion and consequently a reduction in the amount of heavy metal adsorbed at lower pH (Lee, 1999).

The effectiveness of the anionic ligands in the removal of heavy metal ions from aqueous solution seems to be low for the EDTA. Also there may be an inhibition in the adsorption capacity of the substrate in the presence of EDTA at pH of about 4 – 6 for the three metal ions studied. It is likely that the EDTA (with strong chelating property and being a hexadentate ligand)

Table 1: EFFECT OF ANIONIC LIGANDS ON METAL ION REMOVAL

| pH | Ligand – free metal ion solution | | | | | | 0.01M EDTA + Metal ion solution | | | | | | 0.01M Ethylenediamine + Metal ion solution | | | | | | 0.01M Chloride ion + Metal ion solution | | | | | |
|----|----------------------------------|-------|------------------|-------|------------------|-------|---------------------------------|-------|------------------|-------|------------------|-------|--|-------|------------------|-------|------------------|-------|---|-------|------------------|-------|------------------|-------|
| | Co ²⁺ | | Ni ²⁺ | | Cd ²⁺ | | Co ²⁺ | | Ni ²⁺ | | Cd ²⁺ | | Co ²⁺ | | Ni ²⁺ | | Cd ²⁺ | | Co ²⁺ | | Ni ²⁺ | | Cd ²⁺ | |
| | E.C. | A.S. | E.C. | A.S. | E.C. | A.S. | E.C. | A.S. | E.C. | A.S. | E.C. | A.S. | E.C. | A.S. | E.C. | A.S. | E.C. | A.S. | E.C. | A.S. | E.C. | A.S. | E.C. | A.S. |
| 2 | 4.50 | 45.50 | 24.80 | 25.20 | 31.91 | 18.09 | 3.26 | 46.74 | 8.23 | 41.77 | 17.19 | 32.81 | 2.95 | 47.05 | 9.50 | 40.50 | 13.41 | 36.39 | 2.92 | 47.18 | 10.80 | 39.20 | 8.33 | 41.67 |
| 3 | 3.95 | 46.05 | 17.70 | 32.30 | 29.42 | 20.53 | 3.20 | 46.80 | 8.83 | 41.17 | 30.08 | 19.82 | 3.12 | 46.58 | 14.40 | 35.60 | 30.93 | 19.07 | 3.95 | 46.41 | 8.92 | 41.18 | 19.39 | 30.61 |
| 4 | 3.75 | 46.25 | 12.00 | 38.00 | 17.39 | 32.61 | 3.85 | 46.15 | 13.85 | 36.15 | 37.76 | 12.76 | 3.30 | 46.70 | 1.70 | 48.30 | 20.08 | 29.92 | 3.35 | 46.65 | 2.70 | 47.30 | 8.46 | 41.54 |
| 5 | 2.95 | 47.05 | 9.50 | 40.50 | 11.46 | 38.54 | 4.35 | 45.65 | 14.90 | 35.10 | 27.84 | 22.16 | 2.92 | 47.18 | 1.42 | 48.58 | 0.04 | 49.96 | 2.92 | 47.18 | 1.42 | 48.58 | 0.04 | 49.96 |
| 6 | 2.84 | 47.16 | 2.50 | 47.50 | 0.01 | 49.99 | 3.51 | 46.50 | 14.40 | 35.60 | 25.69 | 24.31 | 2.92 | 47.18 | 2.10 | 47.90 | 0.04 | 49.96 | 2.92 | 47.18 | 1.42 | 48.58 | 0.77 | 49.23 |

The initial concentration of all the adsorbates was 50ppm

E.C. = Equilibrium Concentration, (ppm)

A.S = Amount Sorbed (ppm)

It might be that at pH > 6.0 some EDTA molecules get directly bonded with the metal ions to form precipitates, this is in addition to the removal of some metal ions by the substrate. The various EDTA species are often abbreviated as H_4Y , H_3Y^- , H_2Y^{2-} , HY^{3-} and Y^{4-} . It is apparent that H_2Y^{2-} predominates in moderately acidic media (pH 3 – 6). Only at pH values greater than 10 does Y^{4-} become a major component of solution (Scoog et al. 1996). Accordingly, at pH 4 – 6, the predominant EDTA species in solution is H_2Y^{2-} which represents only limited chelation ability. Its full chelation ability would be attained when it is in the form of Y^{4-} which is only possible at pH far higher than 6 (Scoog et al, 1996).

The adsorption capacity of the BPKF – en and BPKF – Cl⁻ are within the same range (Table 1). However, quite remarkable is the effectiveness of the Cl⁻ ion, a monodentate ligand, in the removal of metal ions from solution as compared to other anionic ligands in this study. This might not be unconnected with its small size and high electronegativity in addition to its high electron affinity; it might have a modifying influence on the functional groups of the substrate, to enhance adsorption of the toxic metals.

The free energy of the sorption process was obtained from the equation

$$\Delta G^\circ = RT \ln K_c \quad (\text{Glastone and Lewis, 1987})$$

.....(1)

where K_c is the equilibrium constant, T is the temperature in Kelvin and R is the Universal Gas constant. The values of K_c for the three metal ions were obtained from Khan and Singh plot of $\ln Q_e/C_e$ against C_e (Ikhuoria and Omonmhenle, 2006), where Q_e is the amount of metal ion adsorbed in mg/g and relates to the maximum binding capacity and C_e is the equilibrium concentration. The values of Q_e for Co^{2+} , Cd^{2+} and Ni^{2+} ions were 31.486, 21,678, and 18.295mg/g respectively. In the same vein, the values of K_c determined for the three metal ions – Co^{2+} , Cd^{2+} and Ni^{2+} ions were respectively -0.3176, -0.0688 and -0.05466. The values of ΔG° calculated from the Gibb's free energy equation are +2841.76, +6634.34 and +7201.37KJ respectively for Co^{2+} , Cd^{2+} and Ni^{2+} . These thermodynamic data show that the reaction is non –spontaneous in the forward direction.

CONCLUSION

The efficiency of some anionic ligands in the sorption of some toxic metals using agricultural materials as adsorbent has been investigated in this study. Interestingly, a monodentate ligand (chloride ion) was found to be more effective in influencing metal ions removal. The cobalt ion was found to be more favoured compared to the other metal ions (Cd^{2+} and Ni^{2+} ions). The thermodynamic data reveal the spontaneity of the reaction to be in the reverse direction.

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