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Competitive modeling for the biosorptive removal of copper and lead ions from aqueous solution by Mansonia wood sawdust

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ABSTRACT

Mansonia wood sawdust is applied as a biosorbent for the removal of copper and lead ions from single and binary aqueous solution. The effect of solution pH, electrolyte, metal ion competition and temperature were examined to obtain insight of its application for industrial waste water treatment.

The Langmuir isotherm provided a better fit to experimental data for lead ion sorption with a higher monolayer capacity, while copper ion sorption was best described by the Freundlich and BET isotherms. The combined effect of adsorbing one metal ion in the presence of the other metal ion reduced the adsorption capacity of either metal ion.

In a binary solution, removal of lead ions in the presence of copper ions followed the Langmuir isotherm model while the removal of copper ions in presence of lead ions followed both the Langmuir and BET isotherm models.

1. Introduction

The quest for cheap and cost effective technology for removal of heavy metals from industrial wastewaters loaded with heavy metal ions has lead to the use of materials of biological origin as adsorbents. Biosorption, as this technique is called, is defined as the passive (not metabolically mediated) binding of metals by living or dead biomass. The most popular biosorbents encountered are microbial, bacterial fungal, or algal biomass and lignocellulosic materials (Ho and Ofomaja, 2005, 2006). These materials have been recognized as potential adsorbents for the removal of heavy metal ions from aqueous solution with the view to replacing existing technologies such as precipitation, ion exchange, solvent extraction and liquid membrane for the removal of heavy metal ions from industrial wastewater. This is because all these processes have the limitations in their technical and/or economical viability (Šćiban et al., 2007).

The use of non-living biological materials as biosorbent has been shown to have certain practical advantages over living organisms. For example, microbial growth is inhibited when the concentrations of metal ions are too high or when significant amounts of metal ions are adsorbed by microorganisms (Darnall et al., 1986). Heavy metal ions are known to accumulate on dead cells and agricultural wastes to the same or a greater extent than living cells (Darnall et al., 1986). This is attributed to the changes which occur in the cell structure after cells are dry-killed affect biosorption (Nourbakhsh et al., 1994). Finally maintaining a living biomass during metal ion biosorption is difficult because it requires a continuous supply of nutrients and toxicity of metal towards microorganism may take place (Habib-ur-Rehman et al., 2006).

In living cells, biosorption mechanism could be explained by physical and/or chemical interactions between cell wall ligands and adsorbate by ion exchange, complexation, coordination and microprecipitation (Ofomaja and Ho, 2007). Passive transport mechanisms have been proposed for the diffusion of the metal ion from bulk solution to active sites of the biosorbent (Veglio and Beolchini, 1997), and functional groups such as phosphate, hydroxyl, amino and carboxyl existing on the surface of the adsorbent can bind metals.

Biosorption has been found to be influenced by the presence of other cations present in industrial wastewaters such as sodium and calcium which can produce three possible types of behaviour: synergism, antagonism and non-interaction (Šćiban et al., 2007; Han et al., 2006). It is also common knowledge that industrial waste waters consist of more than one metal ion, therefore, competition of the various metal ions for sorptions sites may occur during biosorption. Therefore, understanding the effect of these

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interactions on the biosorption process for a particular biosorbent type under these conditions provides insight to its application for real wastewater treatment.

The potential sources of copper ion in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, wood pulp production, and the fertilizer industry, etc. In wastewater from a copper wire mill, the average concentration of copper ions is about 800 mg/dm^3 (Panday et al., 1985). Lead ion is introduced into natural waters through various industrial activities such as those from the insecticide, storage battery, and metal plating/finishing industries. In industrial wastewaters, lead ion concentration is in the range of 200–500 mg/dm^3, these values are very high in relation to water quality standards, therefore copper and lead concentrations in wastewaters should be reduced (Ucun et al., 2003).

In Nigeria, about 19,000 ton of Mansonia wood is used both by the paper and furniture industry per annum. In this study, Mansonia wood sawdust, a readily available wood waste from the paper and furniture industry in West Africa, especially Nigeria, is applied as an adsorbent for the removal of copper and lead ions from aqueous solution of both single and binary metals. The effect of electrolyte (Na^+ and Ca^{2+}) on the metal uptake, metal competition for sites on the sawdust surface and temperature on the equilibrium of sorption was examined. Four isotherm models: Langmuir, Freundlich, Brunner Emmert Teller (BET) and Competitive Langmuir (two competing ions) were applied to describe the equilibrium of sorption in this study. A comparison of the linear regression (r^2) and chi-square (χ^2) analysis of the four forms of the isotherm models have been applied to the experimental sorption data from sorption of copper and lead ions on to Mansonia sawdust.

2. Methods

2.1. Materials

Mansonia sawdust used was obtained from a local sawmill in Benin City, Edo State of Nigeria. The sawdust was washed several times with distilled water to remove surface impurities, and this was followed by drying at 100 °C for 24 h. The sawdust was ground and sieved. Sawdust particles used was that retained between the set of sieves: 150–400 μm. The sieved sawdust was then stored in an airtight container.

Lead nitrate ($Pb(NO_3)_2$) and copper nitrate ($Cu(NO_3)_2$) salts were used in the preparation of the salt solutions. Stock solutions of 1000 mg/dm^3 were prepared by dissolving the accurately weighed amounts of $Pb(NO_3)_2$ and $Cu(NO_3)_2$ in 1000 ml distilled water. Experimental solutions were prepared by diluting the stock solution with distilled water.

2.2. Methods

The proximate composition of Mansonia sawdust was determined using methods of the Association of Official Analytical Chemist (Association of Official Analytical Chemists, 1990). The IR spectra of the Mansonia sawdust sample was recorded using KBr disk in conjunction with a Perkin–Elmer infrared spectrophotometer.

2.2.1. Determination of active sites

Acidic and basic sites on sawdust were determined by the acid–base titration method proposed by Boehm (1994). The total acid sites matching the carboxylic, phenolic, and lactonic sites (Boehm, 1994) were neutralized using a 0.1 M NaOH solution while the basic sites were neutralized with a 0.1 M HCl solution. The lactonic and carboxylic sites were determined with a 0.05 M Na_2CO_3 solution and the carboxylic sites were determined with a 0.1 M $NaHCO_3$ solution. The phenolic sites were estimated by difference.

The acidic and basic sites were determined by adding 50 ml of 0.1 M titrating solution and 1 g of sawdust to a 50 ml volumetric flask. The flask was agitated at 25 °C for 24 h. The flask was agitated manually twice a day. Afterward, a sample of 10 ml was titrated with 0.1 M HCl or NaOH solution.

2.3. Effect of solution pH on lead and copper biosorption

Accurately weighed amount (0.25 g) of Mansonia sawdust was added to five 250 ml beakers containing 100 ml of 120 mg/dm^3 of lead and copper ion solutions, each adjusted to pH of 2.0, 3.0, 4.0, 5.0, and 6.0 using either 0.1 M HCl or NaOH solutions. The solutions were stirred at 200 rpm for 4 h at 299 K. The mixtures were centrifuged and the clear supernatant liquids were analyzed for the residual concentrations of lead and copper ions by Atomic Absorption Spectrophotometer.

2.4. Equilibrium studies

Equilibrium experiments were carried out by contacting 0.2 g of Mansonia sawdust with 100 ml of metal ion solution of different initial concentrations ranging from 60 to 140 mg/dm^3. A series of such conical flasks were agitated at 200 rpm and temperature was maintained at 299 K. Equilibrium concentrations of lead and copper ions were determined by Atomic Absorption Spectrophotometer.

2.5. Effect of electrolyte solution

The effect of electrolyte concentration on the amount of lead and copper ions biosorbed onto Mansonia sawdust from solution containing $NaNO_3$ and $Ca(NO_3)_2$ in the concentration range of 0.001–0.100 mol/dm^3 was studied at 299 K. Equilibrium concentrations of lead and copper ions were determined by Atomic Absorption Spectrophotometer.

2.6. Biosorption from binary metal solutions

This experiment was divided into two parts: (i) equilibrium studies as carried out above to examine the biosorption of lead ion at equilibrium (lead ion concentration ranging from 60 to 140 mg/dm^3) in the presence of 60 mg/dm^3 of copper ion in solution, and the biosorption of copper ion at equilibrium (copper ion concentration ranging from 60 to 140 mg/dm^3) in the presence of 60 mg/dm^3 of lead ions in solution (ii) a series of binary solution where the concentration of lead ion is fixed at 60 mg/dm^3 and concentration of copper ion is varied from 0 to 60 mg/dm^3. In another binary system, the initial concentration of copper ion is fixed at 60 mg/dm^3 and the concentration of lead ion is varied from 0 to 60 mg/dm^3. These binary solutions were agitated at 200 rpm for 4 h. Equilibrium concentrations of lead and copper ions in the various binary solutions were determined by Atomic Absorption Spectrophotometer.

2.7. Effect of temperature

This experiment was carried out by contacting 0.2 g of Mansonia sawdust with 100 ml of metal ion solution of different initial concentrations ranging from 60 to 140 mg/dm^3 at 299, 309, 319 and 329 K. The flasks were agitated 200 rpm for 4 h. Equilibrium concentrations of lead and copper ions were determined by Atomic Absorption Spectrophotometer.