

Removal of Copper and Zinc Ions onto Biomodified Palm Shell Activated Carbon

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Abstract—commercially produced in Malaysia granular palm shell activated carbon (PSAC) was biomodified with bacterial biomass (*Bacillus subtilis*) to produce a hybrid biosorbent of higher efficiency. The obtained biosorbent was evaluated in terms of adsorption capacity to remove copper and zinc metal ions from aqueous solutions. The adsorption capacity was evaluated in batch adsorption experiments where concentrations of metal ions varied from 20 to 350 mg/L. A range of pH from 3 to 6 of aqueous solutions containing metal ions was tested. Langmuir adsorption model was used to interpret the experimental data. Comparison of the adsorption data of the biomodified and original palm shell activated carbon showed higher uptake of metal ions by the hybrid biosorbent. A trend in metal ions uptake increase with the increase in the solution's pH was observed. The surface characterization data indicated a decrease in the total surface area for the hybrid biosorbent; however the uptake of copper and zinc by it was at least equal to the original PSAC at pH 4 and 5. The highest capacity of the hybrid biosorbent was observed at pH 5 and comprised 22 mg/g and 19 mg/g for copper and zinc, respectively. The adsorption capacity at the lowest pH of 3 was significantly low. The experimental results facilitated identification of potential factors influencing the adsorption of copper and zinc onto biomodified and original palm shell activated carbon.

Keywords—Adsorption, biomodification, copper, zinc, palm shell carbon.

I. INTRODUCTION

AN increased concentration of heavy metals in the environment is a result of the extensive development of many industries that use heavy metals in the goods/products manufacturing. Copper and zinc are the oldest metals ever used, like a bronze and a brass, and these materials have been very important in the development of human progress. For instance, building construction is the single largest market of copper consumption followed by electronics and electronic

products, transportation, industrial machinery, and consumer products. Copper byproducts from manufacturing and obsolete copper products are easily recycled and contribute significantly to copper supply to industries. However, considerable amounts of copper are discharged into wastewater streams, although at lower concentrations but nevertheless polluting the aqueous environment. Zinc is also a heavy metal, it is also an essential element in bio-molecules and its uptake by living organisms is important. However, excessive concentrations of zinc from metal refining and manufacturing processes wastewaters result in damages to human health causing metabolism disruptions and arteriosclerosis [1]. Conventional technologies used for metals removal of wastewater such as precipitation, coagulation, ion-exchange and reverse osmosis are certainly efficient; however they are also expensive and often generate significant volumes of sludge, solid waste. The final residues are subject to landfill disposal or safe storage, and such practices increase overall stock of heavy metals in the environment. Development of modern technologies in the waste treatment/minimization field is often directed towards utilization of such materials that correspond to the basic requirements: effectiveness and low cost. The major economy sector of Malaysia is production of palm oil that has greatly expanded in the past decades making Malaysia a leading exporter worldwide. Palm shells are generated in great quantities in this sector and along with other byproducts of the production process are disposed as waste. It is only in recent years the research interest to palm shell waste has increased due to the fact that this material was shown to be an excellent source of high quality and low cost activated carbon production. Another plentiful source of low-cost biosorbents is biomass of various microorganisms. It was shown that microbial biomass can successfully remove metal ions from aqueous solutions via mechanisms of biosorption and bioaccumulation [2]-[6]. The objective of our study was to develop a hybrid biosorbent which combines excellent adsorptive properties of the palm shell activated carbon and sorption capacity of the bacterial biomass of *Bacillus subtilis* to remove copper and zinc ions in aqueous solution. In this paper, the results for copper and zinc removal at different pH of the solutions containing varying concentrations of metal ions are presented; also characterization data of the original and biomodified adsorbents are shown.

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II. EXPERIMENTAL PROCEDURE

A. Adsorbents preparation

Palm shell activated carbon (PSAC) was provided by Bravo Green Sdn. Bhd. a manufacturer of the material located in Kuching, Sarawak, Malaysia. The material is obtained using steam in the physical activation process. A particle size range 1.6-2.0 mm was used throughout the experiments.

Bacillus subtilis strain was cultured in nutrient broth (Merck) at 30°C, 220 rpm for 24 hours. The bacterial biomass was separated via 15 min centrifugation at 5000 rpm. The resulting wet biomass was used to biomodify the palm shell activated carbon.

B. Biomodification procedure

About 40 mL of wet bacterial biomass was mixed with 1.2 g of PSAC in a 50 mL centrifuge tube and left on an orbital shaker at 27°C, 45 rpm for 72 hrs [7]. After that the biomodified PSAC was washed, filtered and dried in an incubator at 80°C overnight. The obtained biomodified PSAC material was stored in a plastic container at room temperature and used throughout the experiments.

C. Adsorbents characterization

The original and biomodified palm shell activated carbon BET surface area was measured by N₂ adsorption (77K) using Thermo Finnigan Sorptomatic 1990 series analyzer. The concentration of the surface groups for both adsorbents was measured based on the Boehm titration method (Boehm, 1994). The pH_{pzc} was determined using the so-called drifting method [8]. The results of the characterization data are shown in Table I.

D. Batch mode adsorption

0.15 M NaNO₃ was used as the background electrolyte solution. The metal ions containing solutions were prepared by diluting the respective metal stock solutions to the desired heavy metal concentration range (20 - 350 mg/L). 250 mg of dry original or biomodified palm shell activated carbon was added to 100 mL of test solution in a conical flask and left overnight on an orbital shaker (LabTech) at 150 rpm and 27°C. The measurement of the initial and equilibrium metal ions concentrations was carried out using ICP-OES (Optima 7000DV, Perkin Elmer). Four pH systems were examined: 3, 4, 5, and 6.

E. Adsorption capacity estimation

The experimental data were fitted into Langmuir isotherm model to determine the maximum adsorption capacity (Q_e):

$$Q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (1)$$

where C_e is metal concentration in a solution and b is the Langmuir isotherm constant.

TABLE I

SURFACE CHARACTERIZATION OF ORIGINAL AND BIOMODIFIED PSAC

	Original PSAC	Biomodified PSAC
Surface area, m ² /g	717	689
Max pore volume, cm ³ /g	0.11	0.15
pHpzc	9.25	8.50
Surface groups, meq/g	3.2	3.0

III. RESULTS AND DISCUSSION

A. Copper adsorption isotherms

The experimental data showed good fit for Langmuir adsorption isotherm model, with high R^2 values; the parameters of the model are shown in Table II. Fig. 1 and 2 show the adsorption isotherms for copper removal at different pHs. The adsorption capacity of the original and biomodified PSAC was estimated based on the Langmuir model. The behavior of the isotherms at pH 4 and 5 is quite similar. The values of copper uptake at these pHs are also quite close for the two types of PSAC. However, at pH 3 the uptake of copper is significantly lower, especially for biomodified PSAC. The obtained isotherms also indicate such different response of adsorption process at lowest pH tested.

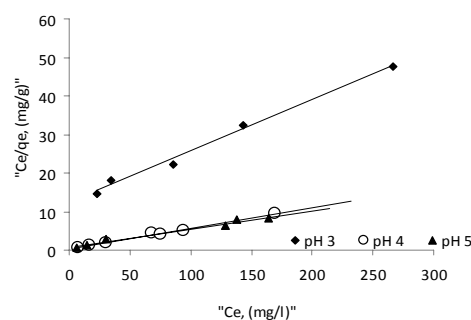


Fig. 1 Langmuir adsorption isotherms for Cu removal on original PSAC

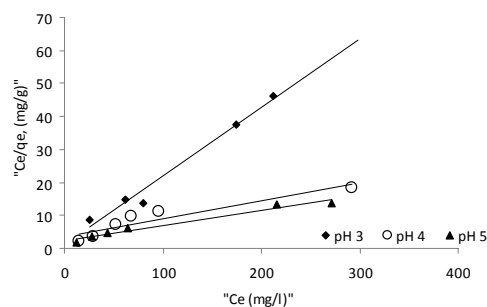


Fig. 2 Langmuir adsorption isotherms for Cu removal on biomodified PSAC

Such difference is attributed to the effect of pH on the copper uptake from the solution. At lower pH the adsorption is subdued due to the competitive adsorption between protons and metal ions. As the concentration of protons increases at

lower pH, the adoption of bivalent copper ions is noticeably slows down as both ions compete for the same biosorbent surface sites. Similar observations were reported for other biosorbents [9]-[11]. The effect of pH is more pronounce for bacterial biomass rather than carbon adsorbent, which is probably due to the higher sensitivity of the bacterial biomass in general to the pH changes of the medium. Thus the biomodified PSAC shows the lowest uptake of copper at pH 3 comprising only 5 mg/g. Comparison of the adsorption capacities for the original and biomodified palm shell activated carbon at pH 4 and 5 shows quite similar level of uptake of copper. Considering that the surface area of the biomodified PSAC is lower than of the original PSAC, the uptake by the former can be considered as improvement. The results for pH 6 are not shown herein because a visible precipitation of copper was observed when copper ions concentration exceeded 150 mg/L.

B. Zinc adsorption isotherms

Fig. 3 and 4 show adsorption isotherms for removal of zinc ions from aqueous solutions obtained using Langmuir isotherm equation onto original and biomodified PSAC. For original PSAC the behavior of the isotherms is similar to the ones described above for copper.

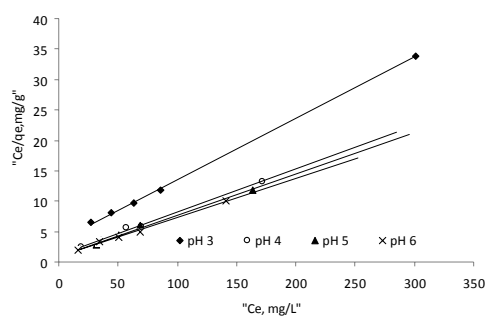


Fig. 3 Langmuir adsorption isotherms for zinc removal on original PSAC

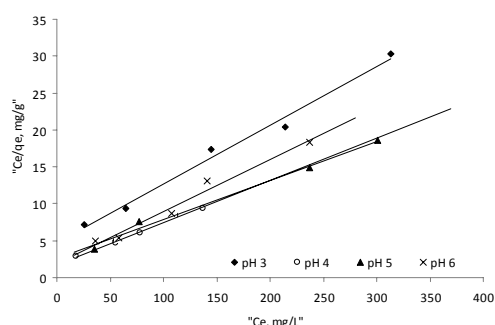


Fig. 4 Langmuir adsorption isotherms for Zn removal on bio-PSAC

However, for biomodified PSAC the response differs especially it is noticeable for pH 6 system. The obtained isotherm infers a decline in zinc ions removal which is possibly associated with the commenced precipitation of zinc

ions at higher pH and increasing initial metal ions concentrations.

In terms of adsorption capacity values, they increase as solution pH increases from 3 to 5 indicating higher affinity of the metal ions to the biosorbent surface at higher pH.

C. Adsorption capacities for copper and zinc removal

Fig. 5 present data on the adsorption capacity obtained for copper and zinc removal onto original and biomodified palm shell activated carbon. The comparison indicates a similar trend for the two metals in terms of effect of pH. The effect of pH is stronger for pH 3 and pH 6 system; thus indicating that an optimal range of pH is between pH 4 and 5. Also the data show that biomodified PSAC can remove more metal ions as compared to the original PSAC at pH 4 and 5.

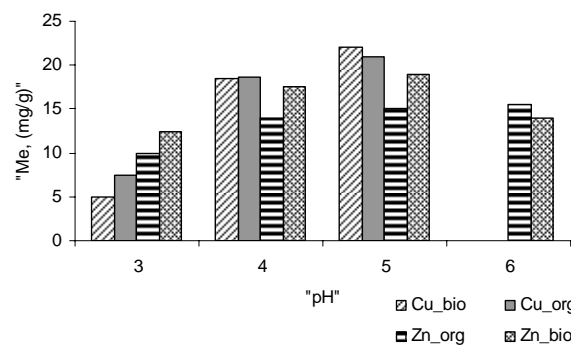


Fig. 5 Adsorption capacities for Cu and Zn removal by original and biomodified PSAC

Table II summarizes adsorption capacity data for the removal of copper and zinc on the biomodified and original PSAC.

	pH	Q_e , mg/g	b	R^2
Cu_original_PSAC	3	7.5	0.011	0.992
	4	18.6	0.16	0.992
	5	21	0.063	0.997
Cu_biomod_PSAC	3	5	0.174	0.979
	4	18.5	0.015	0.888
	5	22	0.019	0.961
Zn_original_PSAC	3	10	0.03	0.999
	4	14	0.06	0.995
	5	15	0.07	0.996
Zn_biomod_PSAC	3	12.5	0.02	0.988
	4	17.5	0.03	0.992
	5	19	0.02	0.993
	6	15	0.04	0.997

The metal ions uptake on the biomodified carbon is higher for both metals; it also increases as pH of the solution increases. This trend indicates that biomodification of the carbon matrix with bacterial biomass has potential to improve adsorption capacity, especially considering that the total

surface area for the biomodified PSAC is lower than that of the original PSAC. Comparison of the adsorption capacities for copper and zinc removal, it could be noticed that zinc shows relatively higher predisposition to be adsorbed on the biomodified PSAC as compared to copper ions. Such observation perhaps relates to the properties of two metals which are quite similar in terms of atomic weight and radius but different in terms of electronegativity. Also, specific interactions between metal ions and surface groups present on the biosorbent surface play important role.

It is believed that the crucial aspect of the research on the development of a hybrid biosorbent is optimization of the biomodification procedure. The research is considered to be promising as the experimental data indicated important aspects of the biomodification procedure which require further modification and optimization to develop a high efficiency hybrid adsorbent for heavy metals removal in wastewaters.

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