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Heavy Metals Removal in Aqueous Solution by Activated Carbons Prepared from Coconut Shell and Seed Shell of the Palm Tree

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Abstract: The purpose of this study is to convert locally vegetal materials such as coconut shell and seed shell of palm tree, which are low-cost, renewable and widely available into inexpensive adsorbent materials for heavy metal copper, lead and zinc removal from wastewater. Both raw materials were chemically activated by phosphoric acid (H_3PO_4). Various parameters such as adsorbent dose, pH and activation temperature of carbon were studied to establish optimum adsorption conditions. The results showed that the rates of adsorption of metals increase with adsorbent dose. The pH variation showed that maximum adsorption capacities were observed at pH 4. The carbons activated at 400°C display the better adsorption capacities. The amount of metal adsorbed on the activated carbons increases in the order Zn, Cu and Pb. Moreover, the presence of other metallic ions in the solution decreases the rate of removal of each of them.

Key words: Heavy metal removal, activation, adsorption, activated carbon

INTRODUCTION

Metal pollution constitutes a danger to health. Indeed, heavy metals are not generally biodegradable and finally accumulate in nature. These toxic metals can also be found in the human organism by the means of the food chain, involving chronic or acute effects then. It is well known that an insoluble complex copper can cause gastro-intestinal problems and a great amount of copper is dangerous for children. Lead causes irreversible brain disorders, influences the production of haemoglobin and modifies the concentration of blood. It can go through the placenta and destroy the nervous system of a foetus (Rachakornkij *et al*., 2003). The vapor inhalation of zinc involves the drying of the throat, causes a cough and a general weakness. Refinement and water treatment technologies require very powerful processes. For example adsorption on activated carbon to satisfy the standards of potability on distributed water (Al-Asheh *et al*., 2000). Unfortunately the use of commercial activated carbon is not always appropriate for the Third World countries because of its very high cost. Therefore, there is a great need to produce activated carbon starting from less expensive materials and available. Many raw materials such as rice husk (Srinivasan *et al*., 1988), groundnut husk (Periasamy *et al*., 1991), *Moringa oleifera* seeds husk (Warhurst *et al*., 1997), tea leaves (Singh and Lal, 1992), sawdust (Raji and Anirughan, 1997) coconut shell (Alaert *et al*., 1989; Manju *et al*., 1998), coconut husk (Briton Bi *et al*., 2006), oil palm shell (Hussein *et al*., 1996; Guo and Lua, 1998, 2000) were used.

This study is a contribution to the problem of heavy metals removal (copper, lead and zinc) in aqueous solution by the use of activated carbon prepared from coconut shell and seed shell of palm tree. The relatively simple mode of preparation of these carbons constitutes one of the characteristics of this work. First, the study presents the technique of preparation of the activated carbons and then it gives their characteristics to finally show their metals adsorption capacity. The dry coconut shell and the seeds shell of palm tree used, were initially scraped with a knife to remove all fibres present at the surface and then crushed using a crushing mill Retsch Germany of the type BB 100 Rosrfrei. The resulting product was washed several times with distilled water to eliminate the water soluble impurities and then dried at 105°C.

MATERIALS AND METHODS

Activated carbon preparation: About 250 g of the small pieces of coconut shell or seed shell of palm tree were mixed with 35 mL of concentrated orthophosphoric acid. The mixture was carbonized at 300°C during 16 h. The

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sample was then withdrawn from the furnace and cooled in a desiccator. After cooling, the sample was rinsed several times with distilled water to pH 6-7. The wet sample was dried at 105°C during 24 h. It was then crushed and filtered. Only size particles of 0.5-0.2 mm were used throughout the study. CA represents the sample obtained from coconut shell and GA, the other one obtained from seed shell of palm tree.

Activated carbon characterization

Ash content: The ash analysis was carried out according to an ASTM method (American Standards Method Technology). Each sample was charred at 650°C in the muffle furnace until no further weight loss was detectable. The samples were weighed before and after calcination. The ash content for each sample was calculated according to the following formula:

$$\text{Ash content} = \frac{m_1 - m_2}{m_1} \times 100 \quad (1)$$

m_1 and m_2 weight of the sample respectively before and after calcinations.

Acidity groups on the surface: The acid groups covering the carbon surface were quantified by using the Boehm (1994) titration method that is widely used by many researchers working on the activated carbon (Rockstraw, 2000). For this study the bases used are sodium hydroxide (NaOH), sodium hydrogenocarbonate ($NaHCO_3$) and sodium ethoxide of (EtONa). The followed procedure is that described by Rockstraw (2000).

Surface area: It was performed according to the method of acetic acid molecule adsorption described by Avom *et al.* (2001).

General procedure of the adsorption test: A percolation of 50 mL of an aqueous solution of metal ion (300 mg L^{-1}) was carried out in a tubular column containing a fixed carbon bed. After 30 min of contact time, the filtrate was collected drop after drop. The initial concentration in metal ion C_0 and the concentration in metal ion of the filtrate C_1 were determined on atomic absorption apparatus (Varian AA20). The results are expressed in terms of rate of adsorption (% of adsorption) of the ions Cu, Pb and Zn, according to the following formula:

$$\text{Adsorption rate (\%)} = \frac{C_0 - C_1}{C_0} \times 100 \quad (2)$$

RESULTS AND DISCUS

Activated carbon characterization: According to data indicated in Table 1, the rates of ash remain relatively weak (lower than 5%). That is a characteristics of carbon obtained from vegetable matters and constitutes an

Table 1: Characteristics of activated carbons

		Acidity Neutralization (meq g^{-1})			
	Ash (%)	NaOH	$NaHCO_3$	EtONa	Surface area (S_L) (m^2 g^{-1})
CA	1.87	0.83	0.13	1.28	98
GA	4.26	0.95	0.18	1.73	95

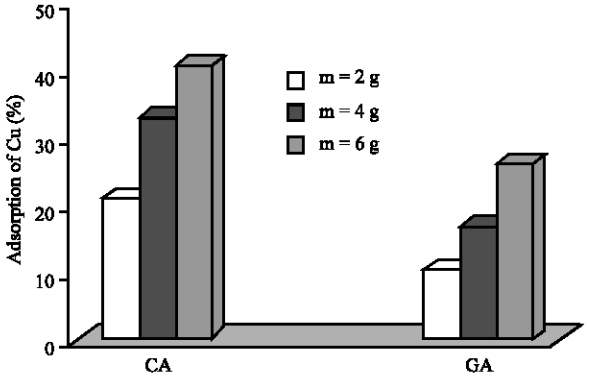

Fig. 1: Effect of absorbent mass on the removal of Cu by CA and GA

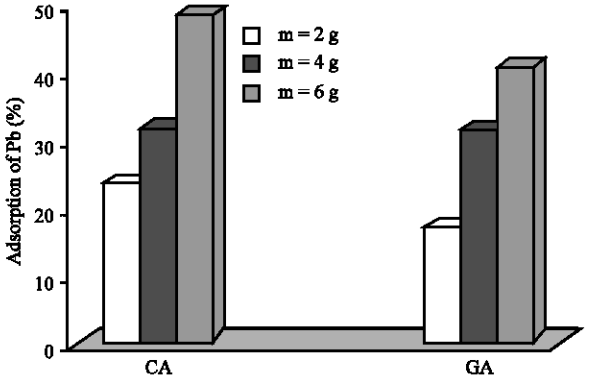

Fig. 2: Effect of adsorbent mass on the removal of Pb by CA and GA

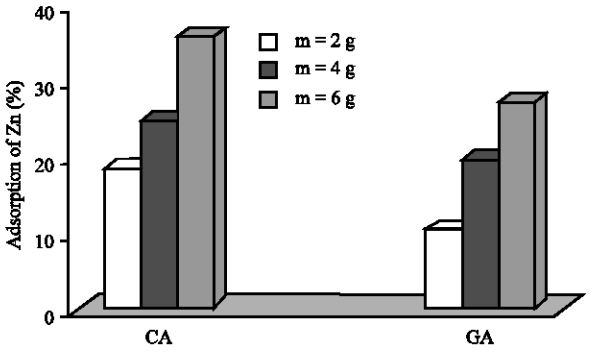

Fig. 3: Effect of adsorbent mass on the removal of Zn by CA and GA

advantage from the point of view of their use in the wastewater treatment. The sample CA is more porous because it has a weaker ash content and also a greater surface area, essential parameter for the adsorbent activity of the activated carbon. The acidity neutralized by $NaHCO_3$ on the surface of carbon CA and GA are 0.13 and 0.18 méq g^{-1}, respectively. This indicates the presence of the carboxylic groups to the surface of coals, which can play a significant role in adsorption. The neutralization of the acids on the surface with NaOH and EtONa, translated the presence of functional group, such -OH; -C = O and -COOH (Boehm, 1994). The values of surfaces area obtained (Table 1) are comparable with those determined by Avom *et al.* (2001). They are relatively weak. That is due to the method, which according to the literature, is less precise and gives values of surfaces area lower than those obtained by the BET method.

Effect of adsorbent mass: Figure 1-3 indicate the influence of the adsorbent mass on adsorption. Both factors are proportional. Many work (Manju and Anirudhan, 1997; Krishnan and Anirudhan, 2003; Mahvi *et al.*, 2005) obtained such results. It seems that the increase in the mass of adsorbent increase the surface area. Several sites of adsorption are thus available to ensure a more significant retention of the metal cations.

Effect of the solution pH: According to Fig. 4-6 the rates of adsorption are weak with the small values of pH (<pH 3). Between pH 3 and 5, these rates increase very quickly to reach a stage with the high values of pH. This is due to the surface charge of the material, which is strongly related to the pH of the solution. The jump in the adsorption capacity observed in the range 3-5 indicate that the pH corresponding to the zero point of charge (pH_{zpc}) of these two materials lies between these values (Ardizzone *et al.*, 1982). The pH_{zpc} is a point at which the surface acidic (or basic) functional groups no longer contribute to the pH value of the solution (Nomanbhay and Palanisamy, 2005). Adsorption of anionic species will be favoured at pH lower than pH_{zpc} and vice versa for cationic species (Rodrigues-Reinoso, 1998).

Moreover, the adsorption of each metal ion on CA and GA as a function of the pH shows a similar tendency but with a low rate of retention on GA_1L_0 and a weak difference between the optimal values of pH. In basic medium, the adsorption of Cu and Pb decreases slightly, probably because of the appearance of the complexes and the insoluble species. As for zinc, after the jumps observed between pH 3 and 4 for CA and between 3 and 5 for GA the rate of retention continues to grow until pH 10. Indeed, the insoluble shapes of zinc appear with the

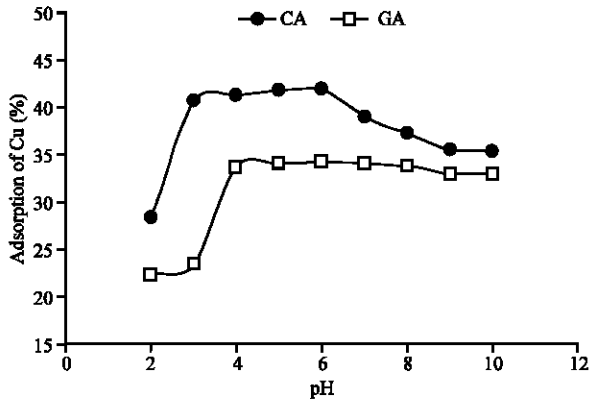

Fig. 4: Adsorption of Cu by CA and GA as a function of pH

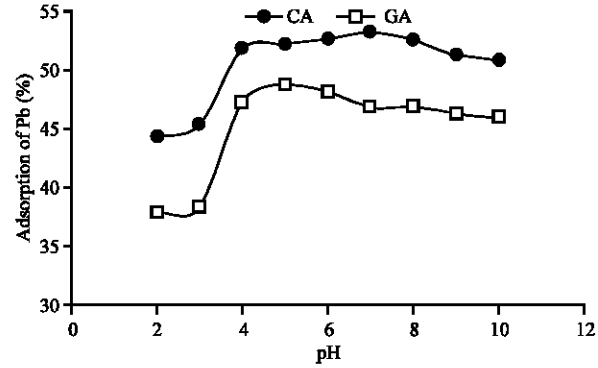

Fig. 5: Adsorption of Pb on CA and GA as a function of pH

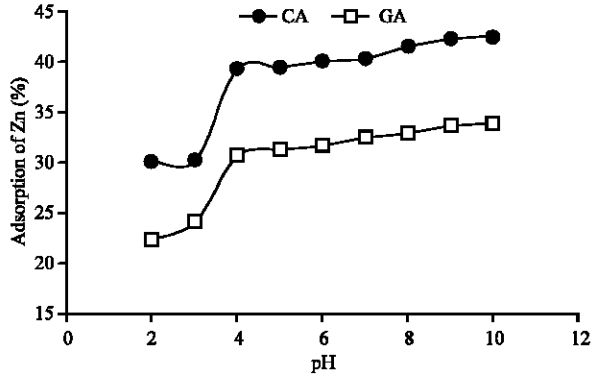

Fig. 6: Adsorption of Zn on CA and GA as a function of pH

pH higher than 11. When the species hydrated, complexed or insoluble take forms, there is competition between adsorption and precipitation. It is then difficult to attribute the increase in the rate of adsorption to the only phenomenon of adsorption. Thus, on the basis of data collected, it seems that the results would be better at pH 4 where precipitation is not dominating on adsorption.

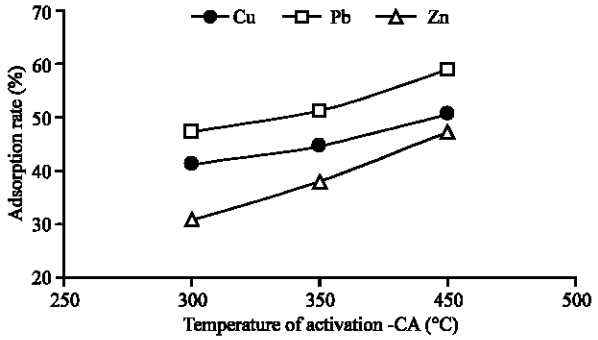

Fig. 7: Adsorption of Cu, Pb and Zn on CA as a function of temperature of activation

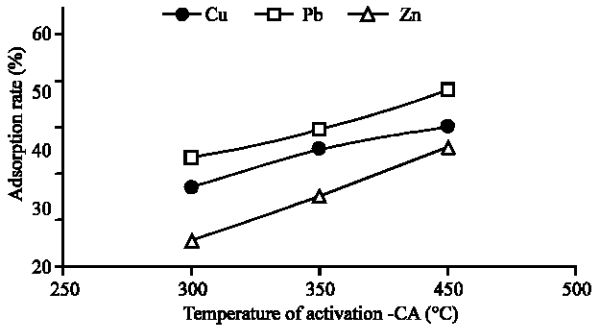

Fig. 8: Adsorption of Cu, Pb and Zn on GA as a function of temperature of activation

Effect of carbon activation temperature: The adsorption rates of Pb, Cu and Zn by CA and GA as a function of the activation temperature are illustrated by Fig. 7 and 8 respectively. It can be noticed that the rise in the activation temperature generates carbons of high adsorption capacities. Indeed, improvements of adsorption rate (19% for Pb, 34% for Cu and 39% for Zn) are observed when the activation temperature of carbons increases from 300 to 400°C. The activated temperature of carbons influences their behaviours. It is known to be one of the significant factors, in the development of the porosity. These results are in a good agreement with those obtained by certain authors (Rahman and Saad, 2003; Deng *et al*., 1997). They indicate that the rise in the temperature of activation would open new pores accessible to the metal ions. The values of surface area indicated in Table 2, illustrate well this proposal.

Selectivity of the metal ions: Table 3 illustrates the adsorption rate of each metal in the presence of the others. Let us note that the simultaneous presence of the three metals in the solution involves a competition during adsorption. Zn is the least supported by the presence of the other metal since it undergoes a fall of its adsorption rate of 33% for CA and 31% for GA. It is however notable that in spite of the competition, all metal are nevertheless adsorbed.

Table 2: Surface area as a function of temperature

Carbons	S_L (m^2 g^{-1})	Carbons	S_L (m^2 g^{-1})
CA (300°C)	98	GA (300°C)	95
CA (350°C)	115	GA (350°C)	103
CA (400°C)	123	GA (400°C)	112

Table 3: Competitive adsorption of metals

	Adsorption rate of metals alone in solution (%)			Adsorption rate of metal in the presence of the others (%)		
Samples	Cu	Pb	Zn	Cu	Pb	Zn
CA	50.64	58.75	47.32	42.36	53.87	31.48
GA	44.23	50.67	40.81	39.25	45.73	28.12

CONCLUSIONS

The results obtained show that the adsorption rates of metals increase with the carbon mass. The optimum value of pH, found for the adsorption of three metals is 4. The activation temperature of carbons is a determining parameter. So the carbons, activated at 400°C have the best adsorption capacities, compared to those activated at the lower temperatures. It also comes out from all the study that, this adsorption follows the order ascending Zn, Cu and Pb. The order observed is largely related to the physicochemical properties of the ions considered. In addition, carbon from coconut shell, gives in general, a better capacity of adsorption than the one from seed shell of palm tree.

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