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Adsorption of iron and zinc on commercial activated carbon

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Commercial activated carbon from local wood was investigated as a suitable adsorbent for the removal of heavy metal ions such as zinc and iron from synthetic and industrial wastewater through batch adsorption process. The initial and final concentrations were determined by absorption atomic spectrometer (AAS). The models of Langmuir and Freundlich were applied to describe adsorption, and Langmuir model is more appropriate to represent the experimental equilibrium. The maximum adsorption capacities of Zn^{2+} and Fe^{2+} calculated by the Langmuir model were respectively 15 and 31 mg/g, with synthetic solution at an initial Zn^{2+} and Fe^{2+} concentration of 5 mg /L. The removal of Zn^{2+} and Fe^{2+} from wastewater was around 70%.

Key words: Adsorption, zinc, iron, activated carbon, Langmuir.

INTRODUCTION

Côte d'Ivoire is a developing country which has a significant industrial growth. These industries release water loaded with heavy metals. These wastewaters are generally not treated prior to discharge into lagoon and sewers and cause serious environmental problems. Pollution from metals is known to be responsible for many health problems (Liu et al., 2008).

Among pollutants, zinc and iron have attracted our attention because; they are the most released by industries. To curb this kind of pollution, a local alternative must be developed by these countries to ensure the health of their inhabitants.

There are several methods of treatment geared towards removing these pollutants from water, such as: filtration, ozonation, clarification, photocatalysis, adsorption, membrane processes, electro coagulation, and chemical processes (Namasivayam and Ranganathan, 1995). Although, the above-mentioned methods are efficient in treating high concentration of heavy metal ions, nevertheless these techniques also have disadvantages including incomplete metal removal, high consumption of reagent and very high cost incurred in the process. For the lower concentration of heavy metal ions, adsorption is a much preferable technique and activated carbon has been widely applied for treating industrial wastewater.

Activated carbons as adsorbents from plant origin have been developed from agricultural by-products, called biosorbent. Crude olive stone was used for adsorption of iron present in industrial wastewater (Nieto et al., 2010). Commercial activated carbon is used for the adsorption of Zn and it depends of the pH of the solution. The adsorption drops at pH < 2 (Ramos et al., 2002). The removal of Zn from water with carbon nanotube was compared to powder commercial activated carbon. The adsorptions were respectively 43.66 mg/g and

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13.04 mg/g (Lu and Chiu, 2006). Adsorption on activated carbon remains one of the mainly used methods for these countries. Several authors (Lalhruaitluanga et al., 2010; Depci et al., 2012; Sekar et al., 2004; Mohan and Singh, 2002; Hajjaji and Arfaoui, 2009) have showed the effectiveness of this type of material and often from plant in treating industrial wastewaters.

The aim of this work is to investigate the removal of zinc and iron from synthetic solution and industrial wastewater with commercial activated carbon from local wood. The adsorption of metal showed two important parameters: initial concentration and pH of solution. These parameters allows for maximizing the amount of adsorbed metals. However, the problems associated with these adsorbents are the regeneration and recovery of the useful materials, which makes them unattractive for wider commercial applications.

EXPERIMENTAL

Adsorbents and chemical

The powder activated carbon supplied by Polychimie Company from Cote d'ivoire, is used as the adsorbent. Activated carbons were produced from wood. The characteristics given are S_{BET}=1400 m^2/g, total pore volume 0.6 cm^3/g and has micropores d ≤ 2 nm and mesopores 2 < d ≥ 50 nm diameters. Metal ions are from these chemicals such as: (Zn $(NO_3)_2$, $4H_2O$) 99%, MERCK, ($FeSO_4$, $6H_2O$) p 99%, Prolabo.

Batch adsorption experiments

Synthetic solutions

Batch adsorption experiments were performed using 250 ml glass bottles. Solutions contain 0.1 g of activated carbon and 20 ml of initial concentrations (C_0) increasing from 100 to 500 mg/l. The suitable pH was adjusted with nitric acid 0.1 M and sodium hydroxide 0.1 M. The glass bottles were sealed with Teflon and were mounted on a shaker. The shaker was placed within a temperature control box and operated at 27°C and 200 rpm for 2 h.

Industrial wastewaters

100 ml of two wastewater samples were collected; S1 and S2. The samples were treated to pH between 5 and 6. We introduced 20 ml of each sample on 250 ml of glass bottles and homogenized with 0.1 g of activated carbon during equilibrium time. The initial and final concentrations of zinc and iron were determined by absorption atomic spectrometer (AAS, Varian AA20) dosing solution up to concentration limits of 1µ/g. The amount of metal adsorbed is calculated as follows:

$$q = \frac{(C_0 - C_t)\,V}{m} \tag{1}$$

where q is the amount of metal adsorbed by activated carbon (mg/g); C_0 is the initial metal concentration (mg/l); C_t is the final metal concentration after filtration (mg/l); V is the initial solution volume (L); m is the activated carbon dose or weight (g).

Isotherm models

The experimental data for metals adsorbed onto activated carbon were approximated by the isotherm models of Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906).
These models suggest the following conditions:

i. Langmuir model supposes a monolayer sorption with a homogenous distribution of sorption sites and sorption energies, without interactions between the adsorbed molecules or ions.
ii. Freundlich model shows lateral interactions between the adsorbed molecules or ions and energetic distribution of sites is heterogeneous, due to the diversity of sorption sites or the diverse nature of the metal ions adsorbed, free or hydrolyzed species. These assumptions resulted respectively to equations below of Langmuir and Freudlich.

$$q = \frac{abC_e}{1 + bC_e} \tag{2}$$

$$q = K_f C_e^{1/n} \tag{3}$$

where C_e is the equilibrium concentration of metal (mg/l); a and b are Langmuir constants; K_f and n are Freundlich constants.

RESULTS AND DISCUSSION

The study of the kinetics of adsorption of iron and zinc was carried out at 27°C on powder activated carbon from commercial sources. The aim is to determine the time required to reach equilibrium carbon adsorption for each metal.

Figure 1 showed the residual concentrations of metals varied slowly and the holding time of 1 h reflected an equilibrium time. Several authors (Babic et al., 2002; Rangel-Mendez and Streat, 2002; Gouli et al., 2008; Ouattara et al., 2012) obtained equilibrium time equal to 1 h or slightly high. The nature of the metal did not influence the equilibrium time of adsorption. A time slot of 1 h 30 m will be used as the equilibrium time for the study of isotherms to be sure that the adsorption phenomena is complete. One of the factors influencing adsorption of metals on activated carbon is the pH. Before recording data for isotherms, pH was adjusted to 7 and 6 respectively for the removal of zinc and iron to maximize adsorption capacity (Ramos et al., 2002; Lu and Chiu, 2006). The predominant species in this case were Zn^{2+} and Fe^{2+}, Fe^{3+}.

Generally, the small adsorption appears at low pH and it is often attributed to a competition between H^+ and metal ion on the same sites. The activated carbon surface has a positive charge and an electrostatic repulsion takes place between the same charge of the cations and the activated carbon. The increase of pH, cause the negative charge density on the surface to

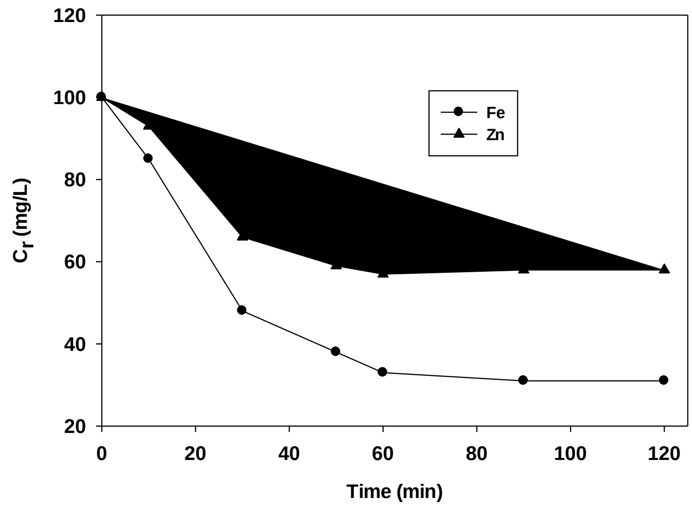

Figure 1. Kinetics of iron and zinc adsorption on commercial activated carbon.

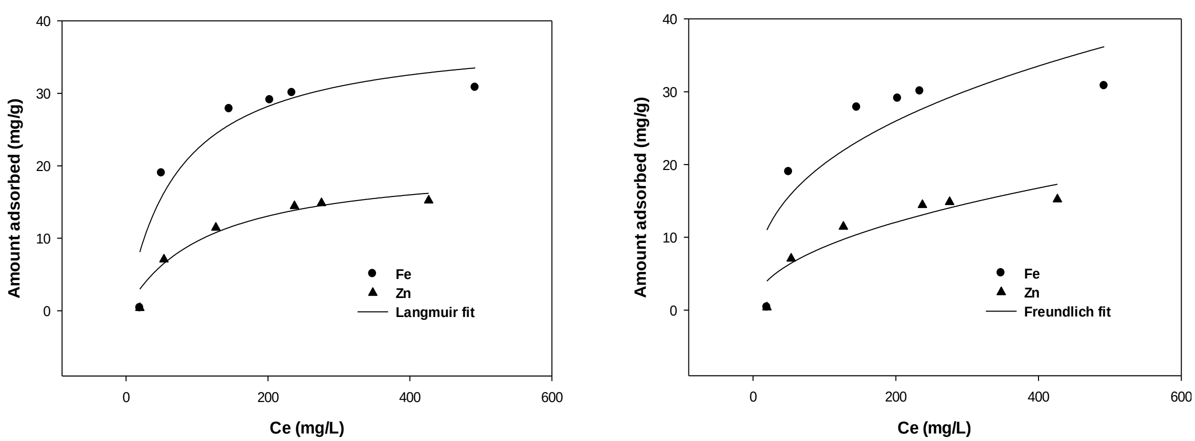

Figure 2. Isotherm adsorption of Zn^{2+} and Fe^{2+} from synthetic solutions at suitable pH for commercial activated powder carbon at 27 °C and Langmuir and Freundlich curves fitted.

increase due to the deprotonisation of positive charged groups on the surface of activated carbon.

In order to show the design of a sorption system to remove zinc and iron from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Two isotherm equations have been tested; Langmuir and Freundlich. The experimental adsorption data were fitted to these isotherm models for synthetic solutions and shown in Figure 2.

The high adsorption values on the commercial powder activated carbon were 31 and 15.2 mg/g respectively for ion and zinc. These values are in the order of metal adsorption from activated carbon. The values of the constants of Langmuir *a, b* and q_m with the correlation coefficients are listed in Table 1 for Zn and Fe. The value of the correlation coefficient is higher with Langmuir model than Freundlich. The Langmuir equation represented the best fit of experimental data than Freundlich isotherm equation. Thus, Langmuir model was suitable to describe this adsorption.

Table 2 shows the initial concentration and final concentration of iron and zinc in wastewater. Activated carbon adsorbed high concentrations of metal. These high rates should not be attributed only to activated carbon but to the very low concentrations of the initial metals contained in these waters. This activated carbon

Table 1. Parameters of the linear representation of Langmuir, and Freundlich models at room temperature for Iron and Zinc adsorption.

Parameter	Langmuir			Freundlich		
	Q_m (mg/g)	b(L/mg)	R^2	Ln k	1/n	R^2
Fe	38.57	0.0137	0.94	1.304	0.3684	0.85
Zn	20.52	0.0087	0.97	-0.026	0.4750	0.93

Table 2. Initial and final concentration of iron and zinc containing in industrial waste water.

Parameter	Initial metal concentration (mg/L)		Metal concentration after adsorption (mg/L)	
	Fe	Zn	Fe	Zn
S1	55.2 (11.04 mg/g)	98 (19.6 mg/g)	12.73 (2.54 mg/g)	25.76 (5.15 mg/g)
S2	47 (9.4 mg/g)	75 (15 mg/g)	11.72 (2.34 mg/g)	20.94 (4.18 mg/g)

is a very good adsorbent for removing these metals in wastewater, because around 70% of metal is removed. After adsorption the wastewaters are good to be rejected due to its low content concentration of metal.

Conclusion

This study showed that the model of Langmuir can be applied for the adsorption of zinc and iron on activated commercial powder carbon. According to this model, this type of carbon has a high rate of metal removal from industrial wastewater and can be used by the local communities to solve their problems of heavy metal pollution. The rate of removal of these metals is concluded to be around 70 %.

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