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Effective removal of Cu^{2+} and Pb^{2+} ions by Zeolite NaY synthesized from M'Batra clay (Cote d'Ivoire)

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Abstract

Water pollution from heavy metals is a particular problem due to their recalcitrance and persistence in the environment. With the development of research, wastewater treatment has reached a certain level. Adsorbents such as zeolite effectively remove metal ions in the water. The main objective of this research is to study the efficiency of zeolite NaY synthesized from M'Batra clay to remove Cu^{2+} and Pb^{2+} ions in aqueous solution by adsorption. The effects of pH solution, initial concentration, contact time and amount of adsorbent on the removal of copper and lead were studied in batch experiments. The characterization of this zeolite NaY and natural clay was done in a previous work. The results showed that the removal of Cu^{2+} and Pb^{2+} ions over zeolite NaY synthetized with clay extracted from M'Batra village (Cote d'Ivoire) and natural clay is very fast in the first 40 minutes and reaches equilibrium around the 60 minute. The retention capacity of copper and lead on zeolite NaY increases with increased with adsorbent dose, with pH and reaches its maximum at pH = 5. The removal rate of Cu^{2+} and Pb^{2+} increases with the mass of the adsorbent, reaches a plateau around 0.5 g and becomes constant. Freundlich and Langmuir adsorption isotherms indicate that the zeolitic support has a very high adsorption capacity of metal ions of Cu^{2+} and Pb^{2+} in aqueous solution. The adsorption isotherm data fitted well to the Langmuir isotherm. In conclusion, the zeolite NaY synthesized from M'Batra kaolin is an effective adsorbent in the removal of Cu^{2+} and Pb^{2+} metal ions.

Keywords: adsorption, equilibrium, zeolite, adsorbent, adsorbate, Freundlich, Langmuir, isotherms

INTRODUCTION

In recent years, we have seen an increasing advance in water pollution and its effects have spurred efforts to reduce pollution (Aksu and Kutsal, 1999). Rapid industrialization has seriously contributed to the release of heavy metals into rivers. The mining industries, electroplating, metal processing, textile and battery manufacturing are the main sources of contamination by heavy metals (Babel and Opiso, 2007, Nwuche and Ugoji, 2008). These activities pollute the rivers and in particular, make them lose their potential value of use (Celik and Demirbaş, 2006, Demirbas and *al*., 2005, Kadirvelu et *al*., 2001). Contamination of aqueous media with heavy metals and dyes is an environmental problem worldwide due to their toxic effects and accumulation in the food chain (Kapoor and *al*., 1999. Alonso and al., 2002, Sternberg and Dorn, 2002). Of these heavy metal ions, the ions of Cd, Zn, Hg, Pb, Cr, Cu, As, etc. have gained importance because of their highly toxic nature, even at deficient concentrations. For example, lead can produce adverse effects on virtually every system in the body. In low doses of Pb (II), children, in particular, are at risk of developing cognitive behavioral function problems (Eubig et *al*., 2010). At high concentrations, Pb causes health problems such as cancer, the toxicity of the liver, kidneys, hematopoietic system and nervous system (Kim et *al*., 2015). Ingestion of copper in the human body beyond the tolerance range may induce toxic effects such as hemolysis, jaundice and even death (Chen et *al*., 2006). (Björn et *al*., 2003) and (Galhardi et *al*., 2004) have shown that copper overload can induce a set of toxicological activities such as hepatocirrhosis, changes in lipid profile, oxidative stress, dysfunction renal and stimulation of the mucous membrane of the digestive tract. Since heavy metals can't be metabolized and bioaccumulative in living organisms, their elimination in water is very important. Current methods of wastewater treatment include precipitation, coagulation/flotation, sedimentation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption and ion exchange. However, these processes have significant disadvantages, such as incomplete metal removal and high operating costs (Cochrane et *al*., 2006). Among the various physicochemical methods for the removal and recovery of metal ions from effluents, adsorption is the most efficient (Poulsen et *al*., 1992; Mavros et *al*., 1994, Ghosh and Bhattacharyya, 2002). The critical aspect of the adsorption process is the ability to regenerate quickly and at a lower cost (Khan et *al*., 2008). The adsorption process at the solid/liquid interface has been widely used for several reasons, mainly because of its efficiency and economy (Gurses et *al*., 2006; Olakunle et *al*., 2018). Porous materials such as clay (Jaber et *al*., 2005), activated carbon (Zhu et *al*., 2009), zeolites (Wingenfelder et *al*., 2005, Deng and Ting, 2005) are still used as ion adsorbents because of their large surface area, large pore volume, and ion exchange. In this study, the choice of the zeolite synthesized from the clay extracted from M'Batra village in Agboville region (Cote d'Ivoire), emanates from its important adsorption and cation exchange properties.

Our objective in this study is to investigate the removal of inorganic pollutants like Cu^{2+} and Pb^{2+} ions by adsorption on the zeolite NaY synthesized from the clay extracted from the M'Batra village. Studied the influence of operational parameters such as metal ion concentration, pH of the solution, contact time and amount of adsorbent. The Langmuir and Freundlich models are used to fit the model isotherm.

MATERIALS AND METHODS

Adsorbents preparation

The adsorbent preparation has already been described in previous work. A certain amount of clay is physically activated in an oven at 680°C for 3 hours. 8.0525 g of this metakaolinite was melted by adding 1.485 g of NaOH at 550°C for 24 hours. Then, the solid products were ground with a porcelain mortar. The resulting product was mixed with a calculated amount of about 17.85 g of sodium silicate and 8.0525 g of water to produce a system of molar composition $SiO_2/Al_2O_3 = 5.3$, $Na_2O/SiO_2 = 0.25$ and $H_2O/Na_2O = 40$. This material was stored at laboratory temperature foraging for 67 hours. Afterwards, the light pink aqueous gel was transferred to a reactor where the hydrothermal crystallization was carried out at 120°C for 24 hours. The precipitate obtained was filtered, washed several times with distilled water to a pH of between 8 and 9 and then dried at 100°C for 24 hours and named zeolite NaY.

Preparation of Cu^{2+} and Pb^{2+} solutions.

We prepared a stock solution of 1000 mg/L Cu^{2+} in distilled water using copper sulfate ($CuSO_4.5H_2O$) of molar mass 249.68 g.mol^{-1}. The distilled water used in our tests is characterized by a pH between 5.3 and 6.6.

The method consists first of all in preparing a stock solution of 1000 mg.L-1 of Pb^{2+} from lead nitrate salt ($Pb(NO_3)_2$) with a molar mass of 331.21g.mol^{-1}.

Cu^{2+} and Pb^{2+} adsorption tests on zeolite NaY

10 ml of a single metal solution and a pre-weighed amount of adsorbent were poured into vials and placed on a MULTISTIRRER6 shaker for 24 hours since equilibrium was reached adjusted with HCl (0.1 N) and NaOH (0.1 N). The samples of the solutions are filtered using a 0.45 μm membrane of porosity. The final concentration of each metal was determined by atomic absorption spectroscopy (AAS).

The experimental conditions maintained for the various operating parameters such as the pH of the suspension, the amount of adsorbent, the contact time and the metal concentration were as follows.

Effect of pH: Amount of adsorbents 500 mg, initial metal concentration 25 mg L^{-1}, RT temperature, 24 hour contact time, pH range 1-9.

Effect of clay mass: initial metal concentration 25 mg L^{-1}, RT temperature, pH_{Cu} 5 and pH_{Pb} 5.4, contact time 24 hours, adsorbent mass 0.1 to 1 g.

Kinetic study: Adsorbents dosage 500 mg, initial concentration of metal 25 mg.L^{-1}, RT temperature, pH_{Cu} 5 and pH_{Pb} 5.4, contact time 20, 40, 60, 100, 120, 140, 180, 240 , 300 minutes.

Adsorption isotherms ions offset the amount of adsorbents 500 mg, temperature RT pH_{Cu} 5 and pH_{Pb} 5.4, contact time 24 hours, initial concentration of metal 5, 15, 25, 50, 100 mg.L^{-1}.

We calculated the amount, Q_e, of adsorbed Cu^{2+} and Pb^{2+} ions per unit mass of adsorbent and the removal rate (%) using the following equations:

$$Q_e = \frac{(C_0 - C_e)V}{m}$$

$$\text{\% of removal} = \frac{C_0 - C_e}{C_0} 100$$

Where

C_o represents the initial concentration of Cu^{2+} or Pb^{2+} in the solution (mg.L^{-1}),

C_e represent the concentration of Cu^{2+} or Pb^{2+} in the equilibrium solution (mg.L^{-1})

m is the mass of the adsorbent (g)

V is the volume of solution (L).

RESULTS AND DISCUSSION

Influence of contact time

The adsorption of Cu^{2+} and Pb^{2+} ions on zeolite NaY according to contact time was studied at laboratory temperature by varying the contact time and keeping constant the other parameters such as the metal concentration, the pH of the solution and the mass of the adsorbent. This parameter was studied between 10 and 300 minutes and the results obtained are presented in Figure 1. The kinetics of elimination of Cu^{2+} and Pb^{2+} ions is a two-step process. At the beginning of sorption (before 40 minutes) the availability of surface sites, as well as the highest motive force for mass transfer, caused the rapid sorption of Cu^{2+} and Pb^{2+}. This rapid sorption phase of these two ions was followed by a slow increase in the amount of sorbed cations (after 60 minutes), due to the progressive occupation of the active sites and the decrease in concentration of Cu^{2+} and Pb^{2+} in the liquid phase or sorption has become less effective (Sljivic et *al.*, 2009; Apiratikul and Pavasant, 2008). It seems that 60 min are needed to reach equilibrium. So we considered that 60 min were taken adequate time for equilibrium. This equilibrium time is confirmed by the work of Krobba et *al.* (Krobba et *al.*, 2012).

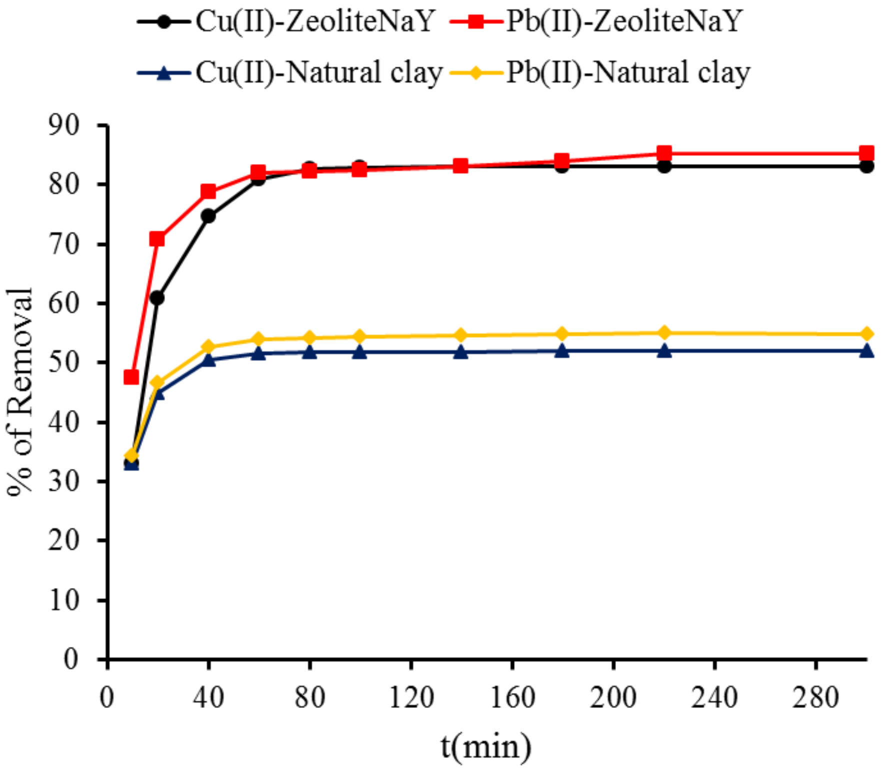

Fig. 1: Influence of contact time on the adsorption of Cu^{2+} and Pb^{2+} metal ions by zeolite NaY. pH = 5 for Cu^{2+} and 5.4 for Pb^{2+}, initial concentration of the metal 25mg.L^{-1}, mass of the adsorbent 500 mg.

Influence of the amount of adsorbent

The adsorbent dose is one of the important parameters in adsorption processes because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate under a given set of operating conditions (Mehdizadeh et al., 2014). To achieve this aim, a series of batch experiments at laboratory temperature by fixing the pH of solutions containing 25 mg.L^{-1} of Cu^{2+} or Pb^{2+} at 5 and varying the mass from 0.1 g to 1.1 g. The results obtained are shown in Figure 2. We have found that the percentage removal of Cu^{2+} and Pb^{2+} increases with the mass of the adsorbent, reaches a plateau around 0.5 g and becomes constant. The increase in the removal rate of Cu^{2+} and Pb^{2+} could be attributed to the larger area and binding sites available as the number of adsorbent increases (Zhi-rong and Shao-qi, 2010, Sen and Gomez, 2011). Once the saturation of the adsorption sites, that is to say, the reduction of the number of sites covered per unit mass, no other adsorption of the metal can be carried out. The removal rate of Cu^{2+} and Pb^{2+} reaches 91% and 93% respectively over zeolite NaY, 53% of Cu^{2+} and 54% of Pb^{2+} over Natural clay. The percentage removal of Cu^{2+} and Pb^{2+} ions is greater on zeolite NaY than on natural clay. This is explained by the higher surface area of the zeolite NaY compared to that of natural clay. Authors like Rida (Rida et *al.*, 2012) in their studies, obtained on masses of zeolite A ranging from 0.05 g to 0.30 g, an increase in the sorption rate of 10% to 80% with a copper solution of a concentration of 1 g/l. Hoda and Fekry (Hoda and Fekry, 2018) in their work to eliminate Cd(II), Fe(III) and Ni(II) ions by natural zeolites have shown that as the adsorbent mass increases, the percentage of metal ion removal also increases. They respectively obtained a maximum elimination of 80.1, 84.5 and 77% of the Cd^{+2}, Fe^{+3} and Ni^{2+} ions for a mass of 1.0 g of adsorbent.

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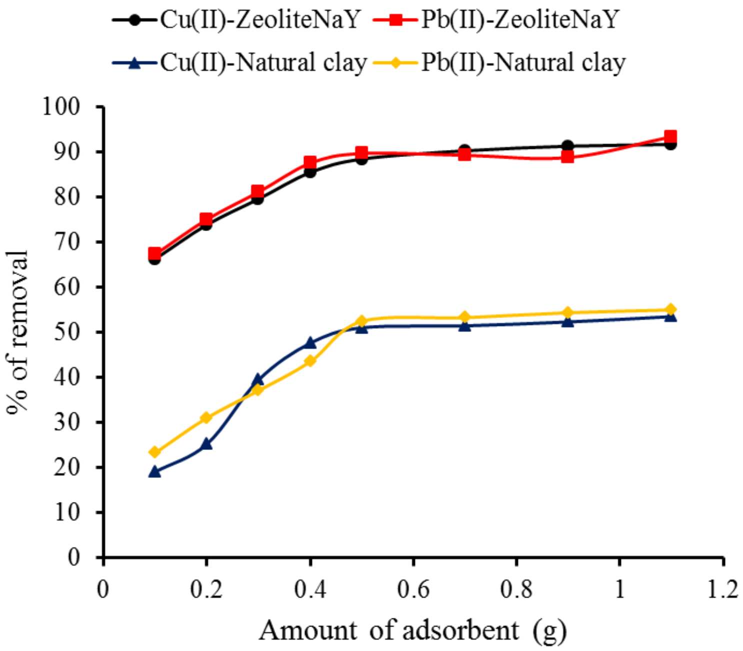

Fig. 2: Effect of adsorbent mass on adsorption of Cu^{2+} and Pb^{2+}. Contact time 24 hours, pH of solution 5; initial concentration of metal 25 mg.L^{-1}

Influence of pH

The influence of pH on the adsorption of Cu^{2+} and Pb^{2+} has been studied in the pH range of 1-9 in steps of 2. The initial pH value of the aqueous metal solution is an essential factor in the adsorption process and control absorption of metal ions at adsorbent - adsorbate interfaces. The results are shown in Figure 3. The adsorption of Cu^{2+} and Pb^{2+} ions was strongly pH-dependent. The adsorption capacity increases reach a maximum at pH = 5 and then decreases. This phenomenon has been observed by several authors (Schawabkeh 2009, Shaobin et al., 2008, Kocaoba et al., 2007) and can be explained as follows: (1) the antagonism between mental and H_3O^+ ions for vacant adsorption sites on adsorbent surfaces; (2) and surface protonation reactions that can lead to positively charged adsorbent surfaces. This results in an increase in repulsive forces between the metal ions and the surface of adsorbents, thereby preventing metal ions from accessing the surface binding sites by producing less adsorption efficiency (Mathialagan and Viraraghavan, 2003, S. Sen and Bhattacharyya, 2008) of the Cu^{2+} metal ions and Pb^{2+}. At pH 7 and 9, metal precipitation occurs as a hydroxide complex. The species are no longer in the cationic form. The surface generated by the precipitation could act as a nucleation site by reducing the apparent solubility product of the hydroxides.

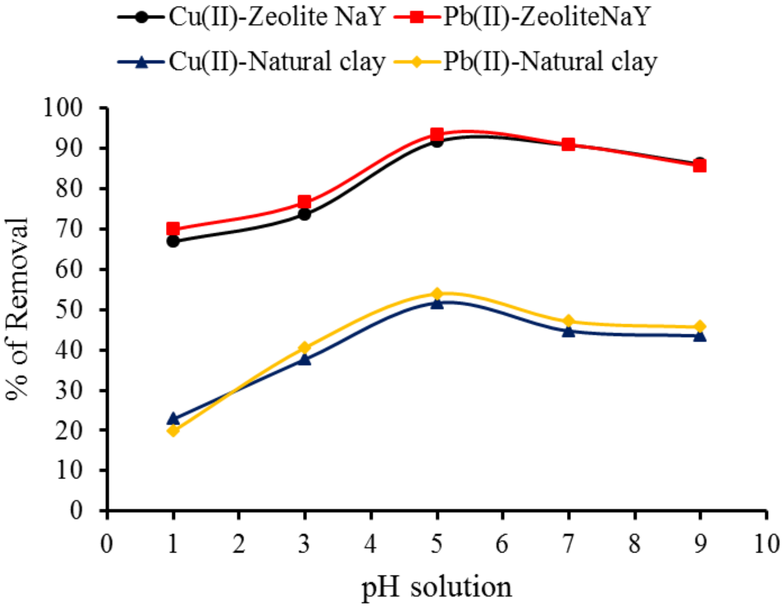

Fig. 3: Influence of pH on the adsorption of Cu^{2+} and Pb^{2+} by zeolite NaY. Contact time 24 hours, initial concentration of metal 25 $mg.L^{-1}$, a mass of adsorbents 500 mg

Adsorption isotherms of Cu^{2+} and Pb^{2+}

In this work, we have relied on experimental data from the Langmuir and Freundlich adsorption isotherms studies. The exploitation of the results according to the Freundlich and Langmuir laws is carried out considering a fixed mass of the adsorbent (0.5 g) and variable concentrations of Cu^{2+} and Pb^{2+} solutions. These data are essential for evaluating the surface properties and adsorbent affinity for Cu^{2+} and Pb^{2+} adsorbates.

The mathematical forms of these two models are given below:

Langmuir model: $\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$

With

q_e: quantity of adsorbed Cu^{2+} and Pb^{2+} ions per unit mass of the adsorbent (mg / g),
C_e: concentration of Cu^{2+} or Pb^{2+} in solution (mg/L) at equilibrium,
q_m: monolayer adsorption capacity of Cu^{2+} and Pb^{2+} ions (mg/g),
K_L: Langmuir adsorption constant (L/mg).

We also used the separation factor R_L (dimensionless) to show the favorable nature of our adsorption system. The adsorption process is favorable when $0 < R_L < 1$. The separation factor is defined as follows:

$R_L = \frac{1}{1+C_o K_L}$

C_o is the initial concentration of Cu^{2+} or Pb^{2+} in the solution ($mg.L^{-1}$)

Freundlich model: $log q_e = log K_F + \frac{1}{n} log C_e$

With:

C_e: concentration of the adsorbate at equilibrium ($mg.L^{-1}$).
q_e: quantity of adsorbate fixed at equilibrium ($mg.g^{-1}$)
K_F: Freundlich adsorption constant ($mg^{1-n} Lng^{-1}$)
n: adsorption constant (without unit)

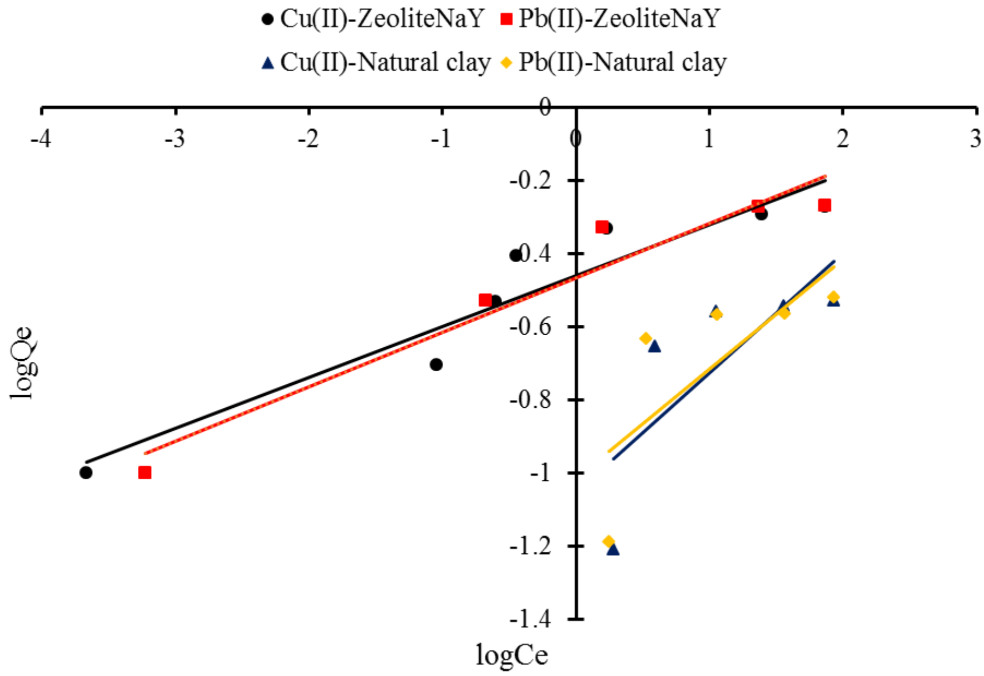

Fig. 4: Freundlich adsorption isotherm of Cu^{2+} and Pb^{2+} ions on natural clay and zeolite NaY at pH 5 at laboratory temperature

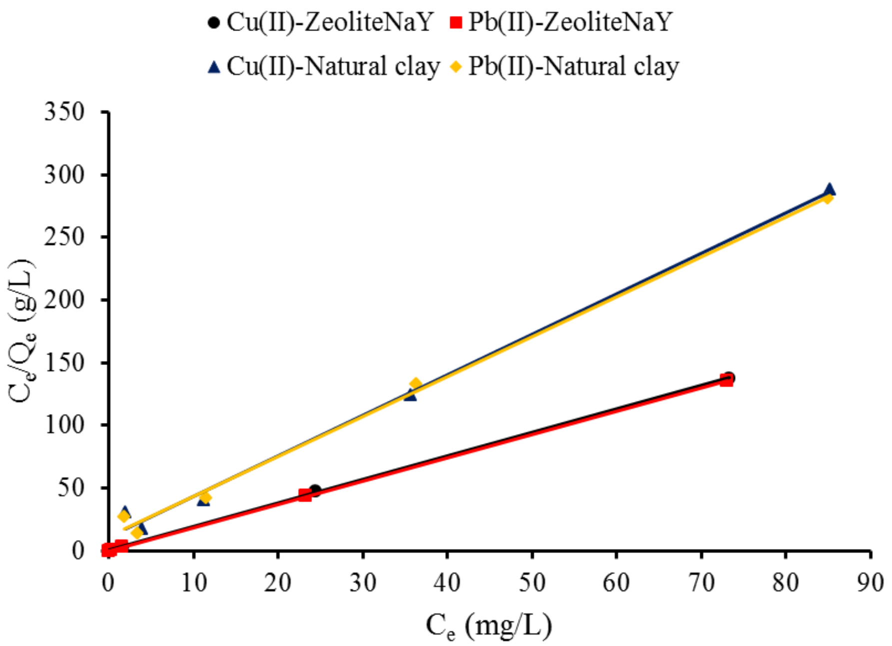

Fig. 5: Langmuir adsorption isotherm of Cu^{2+} and Pb^{2+} ions on natural clay and zeolite NaY at pH 5 at laboratory temperature

Figures 4 and 5 show that the linear forms of Freundlich and Langmuir adsorption isotherms of copper and lead by the zeolite NaY derived from the clay extracted from the M'Batra village of Agboville region (Cote d'Ivoire) and natural clay are satisfactory with good correlation coefficients. The Langmuir and Freundlich models give a good description of the adsorption isotherm. The parameters of Freundlich and Langmuir are summarized in Tables 1 and 2. These parameters related to adsorption capacity and adsorption intensity indicate whether the nature of adsorption is favorable or unfavorable. In this work, the n values of Freundlich isotherms are greater than 1 and indicate that the adsorption intensity is favorable for higher concentration values. The K_F values of Freundlich linear equation (Table 1) also indicate that the zeolite NaY obtained from the clay extracted from M'Batra village in the Agboville region (Cote d'Ivoire) and natural clay extracted from M'Batra village (Cote d'Ivoire) have a very high adsorption capacity of Cu^{2+} and Pb^{2+} in aqueous solution. The R_L values of Langmuir isotherm are 0.91 for copper and 0.8619 for the lead on zeolite NaY and 0.9928 for copper and 0.9932 for lead on natural clay. These values between 0 and 1 suggest that the adsorption process is favorable (Lin et *al*., 2014). Figure 5 shows that the higher the metal concentration, the higher the adsorbed metal content per gram of adsorbent (Qe) because the solute concentration gradient is higher at high concentration; and this provides the driving force necessary for metal ions to move the exchangeable cations to the surface and internal micropores of the zeolite NaY (Taamneh and Sharadqah, 2017, Abadzic and Ryan, 2001).

Table 1: Freundlich adsorption parameters of Cu^{2+} and Pb^{2+} over natural clay and over zeolite NaY

Sample	**Cu^{2+}**			**Pb^{2+}**		
	n	K_F	R^2	n	K_F	R^2
Natural clay	3.0562	0.0888	0.5861	3.3356	0.0970	0.5619
Zeolite NaY	7.1736	0.3470	0.9075	6.6980	0.3419	0.9419

Table 2: Langmuir adsorption parameters of Cu^{2+} and Pb^{2+} over natural clay and zeolite NaY

Sample	**Cu^{2+}**				**Pb^{2+}**			
	q_m	K_L	R_L	R^2	q_m	K_L	R_L	R^2
Natural clay	0.3091	0.2912	0.9928	0.9947	0.3135	0.2733	0.9932	0.9954
Zeolite NaY	0.5333	3.9601	0.9100	0.9998	0.5393	6.4117	0.8619	0.9997

CONCLUSION

In this work, we tested the adsorbent capacity of the zeolite synthesized from the clay extracted from the village of M'Batra in the Agboville region with respect to the elimination of copper and lead ions. The results showed that the retention of these ions (Cu^{2+} and Pb^{2+}) on the zeolite synthesized from the clay extracted from M'Batra village in Agboville region is rapid, 60 min is sufficient to reach equilibrium adsorbent/adsorbate. The amount of Cu^{2+} and Pb^{2+} adsorbed on the zeolite synthesized from the clay extracted from M'Batra village in Agboville region increases with the increase of pH, the amount of adsorbate adsorbed by the zeolitic support used during this equilibrium study is all the more critical as the quantity of adsorbent is high. The modelling by the Freundlich and Langmuir adsorption isotherms shows that for the adsorption of Cu^{2+} and Pb^{2+} is favorable to the high concentrations of the solution, thus the experimental data were better fitted with Langmuir linear model compared to Freundlich linear model.

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