ADSORPTION OF PB (II) IN AQUEOUS SOLUTION ON ACTIVATED CARBON PREPARED FROM ANIMAL BONES

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ABSTRACT

The objective of this study is the removal of lead (II) from water by adsorption on activated carbon, prepared from animal bones. The adsorption efficiency was evaluated for the carbonized raw material at 400 °C and after chemical activation. The adsorption results were about 91.28%, 90.78%, 89.26% at temperatures of 27 °C, 35 °C, 45°C respectively. It was determined that the adsorption system obeyed the pseudo-second order kinetic model by considering the value of the correlation coefficient (R2 > 0.99) with an adsorption constant of 1.45 minute -1 at an ambient temperature of 27°C. The Langmuir isotherm gave a better fit considering the correlation coefficient values (R2 > 0.99). The results indicate that charcoal from carbonized animal bones could be used as an alternative and inexpensive adsorbent for the removal of lead ions from aqueous solutions, when the appropriate conditions are met.

KEY WORDS: Carbonization, Activated charcoal, Animal bone, Adsorption, Heavy metals.

INTRODUCTION

Heavy metals are generally defined as metallic trace elements (ETM) because of their presence in very low concentrations. Heavy metals are considered low density chemical compounds which are highly toxic (Srivastava et al., 2008; Tekaya et al., 2013). In addition, they are defined as metals with atomic masses between 63.5 g / mol and 200.6 g / mol and a density greater than 5 g / cm⁻³ (Turdean, 2011). From a biological point of view, two types are distinguished according to their physiological and toxic effect: essential metals and toxic metals. Essential metals are essential trace elements for many cellular processes and are found in very small proportions in biological tissues (Gemma et al., 2006; Valko et al., 2005). This is the case for copper (Cu), nickel (Ni), zinc (Zn) and iron (Fe). On the other hand, toxic metals have a polluting character with toxic effects for living organisms even at low concentrations. This is the case of lead (Pb), mercury (Hg), and cadmium (Cd)(Terry et al., 2002). Indeed, they lead to greater risk for human health and the

environment (Singh et al., 1997; Jianlong et al., 2004). Heavy metal pollution generally occurs from natural sources caused by natural soil erosion. In addition, this type of pollution is also generated by human resources related to urban and industrial activities as well as using fertilizers in agriculture. These human resources are enormous and their introduction into the environment is very recent (Gao et al., 2013; Callender et al., 2003; Sukandar et al., 2006). Conventional methods for the removal of heavy metals from aqueous media are numerous. Among these methods, the literature includes chemical precipitation, ion exchange, adsorption, flocculation, solvent extraction, electrochemical and biological techniques, membrane processes, ...etc.(Marina et al., 2012; Malterer et al., 1996; Satapathy et al., 2006; Dabrowski et al., 2004; Cochrane et al., 2006). For very low concentrations of metal ions, the sorption technique is the simplest, most available, and most effective. Different types of sorbents are used, such as clays (Merceille et al., 2012), zeolite (Faghihian et al., 1999), activated carbon (Caccin et al., 2013), hydrated metal oxides (Zhang et al., 2015) or titanates, silicotitanates (Shabana *et al.*, 2002; Yavari *et al.*, 2010), and others can be used to remove metal ions from aqueous solutions. Historically, charcoal from animal bones has often been used in sugar refining, fertilizer formulation, black pigment for paint, crude oil refining in the production of petroleum jelly, defluoridation of contaminated water (Pontié *et al.*, 2006; Killedar *et al.*, 1993), copper extraction (Ghrab *et al.*, 2017) etc. This study is devoted to the preparation of an adsorbent, using animal bones as raw material; this material is carbonized at high temperature and chemically activated by phosphoric acid. The final product is used for the removal of metal ions such as Pb⁺² from wastewater.

MATERIALS AND METHODS

In this study, we started with the preparation of the adsorbent, which is charcoal from animal bones. For this, we used slaughterhouse waste (the corpse of a cow) as raw material. The corpse is cut into small pieces and put into a pot to dehydrate it (the water content goes from about 80% to 1-2%), and degrease it, then we proceed with grinding and sieving.

Preparation of metal solutions

- Experimental solutions of Pb⁺² ions with specified concentrations were prepared using analytical reagent grade Pb(NO₃)² that was supplied by Merck during the study.
- The pH values of the solutions were adjusted to the desired values using NaOH with 0.1 N and HCl with 1 N solution. The preparation of all solutions used in this study and the dilutions were carried out using distilled water.

Characterization methods

The specific surface area was calculated using the isothermal equation of Brunauer-Emmett-Teller (BET). The total pore volume (TV) is estimated as the volume of liquid nitrogen adsorbed at a relative pressure (P/P0). In addition, the BJH pore size distribution was determined using the Barrett method. Joyner-Halenda (BJH) applied to the adsorption-desorption hysteresis loop by assuming an open pore pattern of cylindrical shape (Lowell *et al.,* 2004). The volume of mesopores (Vmes) was deduced from the difference between the total pores volume (VT) and misropore volume (Vmic); and the average pore diameter (Dp) is calculated from the specific surface area (SBET) and total pore volume

(VT). In this study, the characterization is carried out using the Quantachrome Nova Win2 device. Before measuring the N₂ adsorption, the sample was degassed for 6 hours at a final pressure of 133.32 × 10^{-4} Pa. The pore area or pore size/volume was estimated from the volume of N₂ (in liquid form) maintained at a relative pressure (P / P0) of 0.99. The sample was then degassed for 6 hours at a final pressure of 133.32 × 10^{-4} Pa.

Experimental

The crushed and siev ed bones are impregnated in 40% phosphoric acid with an acid/bone ratio = 1/2for 72 hours in a 120°C oven (this is the chemical activation), then they are introduced into an adjustable electric tubular oven (quartz tube) of the "PROTHERM" type, to carbonize them at a temperature of 400°C for a contact time of 120 minutes in the presence of nitrogen with a flow rate of 50 ml / min. The carbon obtained were cooled to room temperature, then rinsed and washed several times with 1N acid solution and distilled water until the pH is constant, to remove any residue from the carbonization. The coals thus washed and rinsed and are dried at 105 ° C for at least 8 h in an oven. then cooled in a desiccator and kept away from the air in sealed vials until the characterization tests.

Batch mode adsorption experiment

In order to optimize the experimental parameters of the Pb⁺² ions adsorption processes, batch experiments were performed at three temperatures (27°C, 35°C and 45°C). The influence of operating parameters such as pH value, adsorbent quantity, initial adsorbate concentration, equilibrium time, adsorbent dosage was studied. A quantity of adsorbent was mixed with 100 ml of metal ion solution (Pb⁺²) at different concentrations (100 - 700 mg/L) for a contact time of 10 to 280 minutes. All adsorption experiments were performed in Erlenmeyer flasks (250 ml capacity). The obtained solutions were stirred at a stirring speed (250rpm) on a rotary shaker for a contact time of 0 to 280 min. After the adsorption process, the adsorbent was separated by filtration and the residual concentration of lead and zinc ions was determined by atomic absorption spectroscopy (AAS) (PYE UNICAM SP9). The amount of Pb(II) ions removed by the adsorbent phase qe (mg/g) was calculated from the expression (equation(1)) :

$$Qe = V \times (C0 - Ce)/m$$
 ... (1)

Where: C0 is the initial concentration of heavy metal solution (mg/L), Ce : is the equilibrium concentration of heavy metal solution (mg/L), m: mass of the adsorbent in g ,V volume of the mixture in ml, Qe : adsorption capacity at equilibrium.

Adsorption kinetic studies

Few sorption models were used to evaluate the equilibrium adsorption processes. Langmuir sorption theory described the homogeneity distribution of adsorbed molecules on sorbent active sites (Ali *et al.*, 2019) and is given by the following linear equation:

$$\frac{Ce}{qe} = \frac{1}{qL KL} + \frac{Ce}{qL}....(2)$$

where :qe (mg/g) and Ce (mg/L) are the quantity of solute adsorbed per unit mass of adsorption and equilibrium solute concentration in the bulk solution. K_L (L/g) is constant while q_L (mg/g) is monolayer adsorption efficiency. The dimensionless constant, R_L provide appropriate articulation of Langmuir isotherm expressed as:

The identification of the parameters specified in this equation (3) has been previously described in the literature ((Bayat *et al.*, 2002; Argun *et al.*, 2008). The Freundlich isotherm assumes heterogeneous, and multilayer adsorption occurred on the adsorbent surface calculated using Equation 4:

$$\operatorname{Ln} \operatorname{qe} = \frac{1}{n} \ln \operatorname{Ce} + \mathrm{K}_{\mathrm{F}}.....(4)$$

Where: K_F is Freundlich equilibrium constant, n is an empirical constant and others, as stated in Eq.4. A slope of (1/n) was derived from a plot of ln qe vs ln Ce : indicates the intensity of the process of adsorption (Lachebi *et al.*, 2016). K_F (mg/g) is the isotherm constant.

Adsorption Kinetics Modeling

In order to examine the mechanism of adsorption processes, the pseudo first order adsorption and the pseudo second-order adsorption were used to adjust kinetic experimental data.

Pseudo First-Order Model

The pseudo first-order rate expression of Lagergren is usually described by the following Equations (5) and (6) [31].

$$dqt/dt = K_1(qe-qt) \dots (5).$$

where qe is the amount of lead adsorbed on the adsorbent at the equilibrium time (mg/g), qt is the amount of lead adsorbed on the adsorbent at time t (mg/g) and K₁ is the rate constant of pseudo first-order adsorption (1/min). Integrating and applying the boundary condition, for t = 0, qt = 0 and for t = t, qe = qt, Equation (5) takes the following form:

 $\frac{1}{qt} = \frac{K1}{qet} + \frac{1}{qe}.$ (6)

where K_1 was determined from the slope of linear plot of 1/qt against 1/t.

Pseudo Second-Order Model

The pseudo second-order mechanism for adsorption is shown in Equation (7) (Wu *et al.*, 2001; Antonioa *et al.*, 2007).

$$\frac{dq}{dt} = K_2(qe - qt)^2....(7)$$

where qt is the adsorption capacity at time t (mg/g), K_2 is the rate constant of pseudo second-order adsorption (1/min). Integration and applying the boundary conditions, for t = 0, qt = 0 and for t = t, qe = qt, Equation (7) takes the following form:

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{1}{qe} t....(8)$$

If the second order kinetic model is applicable, the plot of t /qt against t of Equation (8) should give a linear relation ship from which qe and K_2 can be established.

RESULTS AND DISCUSSION

Characterization of adsorbent

The knowledge of the physico-chemical characteristics of carbon, whatever the method of preparation and the type of thermal and/or chemical activation carried out, is necessary for the understanding of many phenomena such as adsorption, desorption, ion exchange and others (Dragana *et al.*, 2019).

Textural characteristics

Figure 1 shows that the isotherm adsorptiondesorption of N2 on the prepared activated carbon is of type II (based on the classification of IUPAC). The values of the different textural parameters are mentioned in Table 1.

The result of table 1 showed that the BET surface area of the prepared activated carbon is $171,948 \text{ m}^2/\text{g}$, low in comparison with other coals where the



Fig. 1. N2 adsorption-desorption isotherm (77 K) of the prepared adsorbent.

 Table 1.
 Textural parameters of the activated carbon prepared.

Textural settings	value	
Specific surface (SBET) Total pore volume (VT) Average pore diameter (Dp)	171,948 m²/g 0,515 cm³ /g 80,93 nm	

specific surface area exceeds 400 m²/g (Mukhin *et al.*, 2014) but it is large compared to that found when the bones were calcined at 800 °C for 2 hours (72 m²/g) (Ghrab *et al.*, 2017). While the surface of this adsorbent has a pore size is greater than 50nm which explains why the pores are large (macroporous), this is the expected result when using carbonization with chemical activation (Duca *et al.*, 2018).

Adsorption experiments

In general, the removal of metal ions from an aqueous solution by adsorption is effective as under well-defined experimental conditions. It is therefore important to study the influence of some experimental parameters (such as pH of the solution, adsorbent dose, contact time, initial concentration of metal ions,....ect.) on the adsorption capacity of a given adsorbent.

Effect of pH

The effect of pH on the removal of Pb (II) ions from aqueous media is a very important factor [36]. Thus, it is one of the most critical parameters in the process of adsorption of metal ions from aqueous solutions (Mouflih *et al.*, 2006). Its influence on the heavy metal ions affects not only the surface charge of the adsorbent (Figure 2), but also the speciation of heavy metals in solution. Metal cations in aqueous solution can be converted to different insoluble hydrolysis products hydrolysis products due to the change in pH (Keles *et al.*, 2010; Weng *et al.*, 2004). The adsorption of lead ions increased significantly with the pH value (3 to 4). The results can be explained on the basis of the competition between Pb (II) and H_3O^+ ions for adsorption sites on the the prepared charon. At low pH values, the adsorbent surface would also be surrounded by an excess of H_3O^+ which decreases the interaction with the prepared charon surface sites by repulsive forces (Allen *et al.*, 1989), showing weak adsorption of Pb (II) ions. However, the best results are given for pH=5 which is reported by previous studies (Mouflih *et al.*, 2006). For pH above 5 (pH=7,8), the adsorption capacity decreases due to the precipitation of Pb (II) ions in the form of hydroxide form



Fig. 2. Effect of pH on the amount of lead adsorbed on prepared carbon. [prepared carbon] = 10g/L, [Pb⁺²]= 100 mg/L, T= 27°C and w =250 rpm.

Effect of adsorbent dosage

The increase in adsorption capacity (Qe) as a function of the dose of adsorbent, is due to a high availability of active sites, which facilitates the fixation of metal ions in the sites (Cechinel *et al.*, 2014). From a mass of 2.5 g of adsorbent (Fig. 3), the concentration of lead at equilibrium tends to stabilize with the appearance of a plateau of saturation beyond this mass, which gives a decrease



Fig. 3. Effect of the amount of prepared carbon on the adsorption of Pb (II) ions: [Pb⁺²]= 100 mg/L, T= 27°C, w =250 rpm and pH=5.

in the capacity of adsorption of lead, up to a value of 7.12g/mg for a quantity of 10g/l of adsorbent. While the maximum value is marked for a dose of adsorbent of 2.5g/l is equal to 29.8 mg/g. The operating dose in the subsequent experiments is 2.5 g.L⁻¹.

Effect of the initial concentration of lead ions

The removal rate of metal ions is of great importance for the development of adsorption technology (Figueiredo et al., 2010). In order to establish the equilibrium time for the maximum consumption and to know the process of adsorption kinetics at different initial concentrations from 100 to 700 mg.l⁻ ¹ of Pb (II) ions by the prepared adsorbent, operating in the contact time ranging from 10 to 280 minutes. Figure 4 shows that the adsorption efficiency of Pb (II) ions increases with time and initial concentration. The higher initial rate of sorption may be due to an increase in the number of adsorption sites available at the initial stage of the adsorption process which results in an increase in the concentration gradient between the solute in solution and the solute on the surface of the adsorbent. This concentration gradient is reduced with prolongation of the contact time due to the accumulation of Pb (II) ions on the vacant adsorption sites which leads to an invariable adsorption rate (Ghodbane et al., 2008; Unuabonah et al., 2007; Futalan et al., 2011; Hamdaoui et al., 2008). The remaining free surface sites are difficult to be occupied due to repulsive forces between the adsorbed Pb (II) ion and the liquid phase (Lian et al., 2009). The increase in sorption capacity is proportional to the initial concentration, this is caused by strong attractive forces between the lead ions and the functions that exist on the surface of the



Fig. 4. Effect of concentration on the adsorption kinetics of Pb (II) ions by the prepared adsorbent: [Adsorbent]= 2,5g/L, T= 27°C, w =250 rpm and pH=5.

prepared adsorbent (Duca *et al.*, 2018). The time required to reach equilibrium as a function of the initial concentration of Pb (II) ion is around 240 minutes. However, the experimental data was measured at 280 minutes to achieve full equilibrium. The adsorption capacity at equilibrium increases from 29.8 to 182.56 mg.g⁻¹, respectively, with increase of the initial Pb (II) ion concentration from 100 to 500 mg.l⁻¹. This finding indicates that the initial concentration of Pb (II) ions plays an important role in the adsorption of Pb (II)(Fu *et al.*, 2012).

Effect of temperature

Measurement of residual lead (II) concentrations at different temperatures (27, 35, and 45°C) allowed the development of adsorption isotherm curves (Figure 5). At 27°C, the maximum adsorption capacity on the prepared charcoal is 182.56mg/ g.Increasing the temperature of the samples at 35 and 45°C, results in a decrease in the adsorption of lead (II) on this prepared charcoal; at 45°C, the capacity was reduced to a value of 178.52mg/g from the maximum capacity at 27°C. With increasing temperature, the stability of the bonds between the active sites of carbon and lead would decrease. This negative effect of adsorption at high temperature, is reported by several authors on different materials and pollutants: for example, Bereket et al. (1997), in the study of heavy metal adsorption on bentonite and Ayhan Demirbas (2008) in the study of heavy metal adsorption on agricultural waste.



Fig. 5. Adsorption isotherms of lead (II) on prepared carbon: pH=5, [adsorbent]= 2,5 g/l and w=250 rpm,[Pb⁺²]=500mg/l.

Kinetic studies

The kinetics of adsorption explains the variation of adsorbate uptake as a function of time. parameters provide important information for modeling and designing the adsorption process. To this end, adsorption data were analyzed with two kinetic models: pseudo-first order and pseudo-second order. The parameters K and Qm can be obtained directly from the interceqtion and slope of the plot of 1/qt as a function of 1/t or(t/qt) as a function of t (Fig. 6,7). According to Table 2, the pseudo-second order kinetics model obtained a larger correlation coefficient (R2 > 0.99) and with Qm =185.18 mg/g. The result shows that the pseudo-second order kinetic model was more representative than the other kinetic model for the simulation of kinetic data at differe nt temperatures.



Fig. 6. Pseudo-first - order kinetic plots, for the removal of Pb(II) at different temperatures.



Fig. 7. Pseudo-second-order kinetic plots, for the removal of Pb(II) at different temperatures.

Linearization of the adsorption isotherms of lead (II) on this coal prepared at different temperatures (27, 35 and 45°C) (application of equations (2 and 3) of the Langmuir and Freundlich models) showed (Figures 4, 5), the applicability and compatibility of

these models to equilibrium data. The constants deduced from the linearization are grouped in Table 3. Correlation coefficients greater than 0.97 indicate that the resulting isotherms are correctly described by both linearized Langmuir and Freundlich models. The adsorption constants at 27 °C are larger than those at 35 and 45 °C. This reflects the greater strength or affinity existing between charcoal and lead (II) at 27 °C. The exothermic effect of adsorption is confirmed by these constants. Table 3 shows that the correlation coefficient of Langmuir model is higher than Freundlich model, which shows that



Fig. 8. Modeling of adsorption isotherms of lead (II) on carbon prepared according to the Langmuir equation



Fig. 9. Modeling of adsorption isotherms of lead (II) on carbon prepared according to the Freundlich equation

Model of adsorption Pseudo First-Order Model	Parameters		Température (°C)	
	Qe(mg/g)	27	35	45
	K1	192.30	185.18	181.81
	R2	0.88	0.75	0.6
		0.9519	0.9471	0.8056
Pseudo Second-Order Model	Qe(mg/g)	185.18	172.41	172.41
	K2	1.45	1.12	0.84
		0.9961	0.9989	0.0084

Model of adsorption	Parameters		Température (°C)		
		27	35	45	
Langmuir	$q_{I}(mg/g)$	185.18	181.81	178.57	
0	K,	0.034	0.012	0.01	
	R^{2}	0.9945	0.991	0.9945	
	R_{L}	0.055	0.16	0.16	
Freundlich	1/n	1.99	2.0685	2.082	
	KF	0.029	0.011	0.0058	
	R ²	0.9826	0.9847	0.985	

Table 3. Deduction of the Adsorption Constants of the Studied Models

this adsorption is better described by Lagmuir model, as well as the RL values obtained at a concentration of 500 mg/l at different temperatures (27°C, 35 and 45°C) are respectively 0.055, 0.16 which implies that the adsorption is favorable by this model and which is due to the effect of the phenomenon of diffusion and sorption in the pores (Goswami *et al.*, 2005) on the other hand the value of 1/n (Frandlich model) greater than unity means that the adsorption is unfavorable. Therefore, it can be said that the adsorption system of lead ions on the studied prepared adsorbent confirms the Langmuir model better due to the high value of the correlation coefficient.

Thermodynamic quantities of the adsorption equilibrium

An increase in temperature resulted in a decrease in the adsorption capacity of lead (II) for the studied activated carbon. This exothermic phenomenon of adsorption, can also be justified by the classical thermodynamic quantities enthalpy (Δ H°), entropy (Δ S°) and free energy (Δ G°).determined by equations (9 and 10) (Al-Ghouti *et al.*, 2005):

Ln (K/T) = [Ln (KB/hp) + $\Delta S^{\circ}/R$] - ($\Delta H^{\circ}/R$)(1/T) ... (9) $\Delta G^{\circ} = \Delta H^{\circ}$ - T ΔS° ... (10)



Fig. 10. Determination of thermodynamic parameters.

Table 4. Determination of Thermodynamic Parameters

Temperature	ΔH°	ΔS°	∆G°
(°C)	(KJ/mol)	(KJ/mol.K)	(KJ/mol)
27 35 45	-24.96	-0.324	72.24 74.832 78.072

Where : K : apparent second order rate constant (g.mg⁻¹.min⁻¹); T : temperature (K); KB: Boltzmann's constant (1.3807x10⁻²³j/K); hp: Planck's constant (6.6261x10⁻³⁴J S);

 ΔS° : variation of entropy (J) ; ΔH° : enthalpy variation (J); ΔG° : variation of free energy (J) ; R : constant of perfect gases (8.314 J/mol.K).

The values of ΔH° and ΔS° are calculated from the slope and intercept of Ln(K/T) versus 1/T (Figure 6). The negative values of ΔH° and ΔS° (Table 3), show that the adsorption reaction is exothermic and that during adsorption, the degree of freedom of the adsorbed species decreases at the solid/solution interface. The free energies, ΔG° , are positive, showing that the adsorption process of lead (II) on the studied activated carbon, is non-spontaneous which would assume chemical adsorption.

In order to compare the adsorption capacities of heavy metals with various materials studied by several researchers, we tried to summarize the different adsorption results with the most interesting operating parameters. from table 5 we note that the adsorption of Pb + 2 with the material used in this work gave good results compared to other work with a maximum adsorption capacity = 182.56mg / g.

CONCLUSION

This study was devoted to the adsorption of lead (II) contained in water by an adsorbent from carbonized animal bones. The choice of lead (II) is motivated by

Adsorbent	Adsorbate		Adsorption conditions		
		T[°C]	Q[mg/g]	pН	
Bone char	(Cd+2, Ni+2,Zn+2) ternary mixtures	30	108.09(Cd+2) 23.70(Ni+2) 63.63(Zn+2)	5	[53]
Pin cone	Cu(II) Cd(II) Cr(VI) Pb(II)	- - -	33.35 50 68.03 95	5.4 5.4 2 5.4	[54]
Eggshell membranes of differentbirds (ostrichquail, duck and chiken)	Cr(VI)	25	259	2	[55]
Konjac starch Magnetic graphemeoxide nanocomposites	Pb+2 As(V)	60 -	- 3	22.25 69.44	[56] [57]
Nanogoethite Actived carbon prepared from cow bones	U(VI) Pb(II)	25 27	4 5	104.22 182.56	[58] This study

Table 5. Comparison of heavy metals uptake with different materials

its high toxicity and its worldwide occurrence in water and soil. The adsorption capacity was examined at various parameters: pH, adsorbent dose, initial ion concentrations, temperature and contact time.

The maximum adsorption capacities of lead(II) ions are: 182.56mg/g, 181.52 mg/g and 178.14 mg/g for the temperatures 27°C, 35 and 45°C respectively for the optimal conditions: pH=5, adsorbent dose =2.5g /l, initial lead concentration=500mg/l and adsorbent-adsorbate contact time=240minutes.

The adsorption tests are in good agreement with the Langmuir and Freundlich adsorption models. On the other hand, the adsorption kinetics is slow and follows suitably the pseudo-second order model. The thermodynamic study found that the adsorption process is non-spontaneous, exothermic with a high affinity for lead on animal bone charcoal.

Based on these results, when the appropriate conditions are carried out, animal bone charcoal can be used as an effective and economically viable adsorbent to remove lead(II) from aqueous solutions.

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