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Activated carbon from molasses efficiency for Cr(VI), Pb(II) and Cu(II) adsorption: A mechanistic study

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ARTICLE INFO

Article type:

Research article

Article history:

Received October 2016

Accepted January 2017

July 2017 Issue

Keywords:

Molasses

Activated carbon

Phosphoric acid

Adsorption

Metal ions

ABSTRACT

Activated carbon was prepared from molasses, which are natural precursors of vegetable origin resulting from the sugar industry. A simple elaboration process, based on chemical activation with phosphoric acid, was proposed. The final product, prepared by activation of molasses/phosphoric acid mixture in air at 500°C, presented high surface area (more than 1400 m²/g) and important maximum adsorption capacity for methylene blue (625 mg/g) and iodine (1660 mg/g). The activated carbon (MP2(500)) showed a good potential for the adsorption of Cr(VI), Cu(II) and Pb(II) from aqueous solutions. The affinity for the three ions was observed in the following order Cu²⁺ > Cr⁶⁺ > Pb²⁺. The process is governed by monolayer adsorption following the Langmuir model, with a correlation coefficient close to unity.

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Capsule Summary: The study present the result of adsorption of Cr(VI), Cu(II) and Pb(II) by an activated carbon prepared by chemical activation of molasses with phosphoric acid. A good potential for adsorption of three ions was observed.

Cite This Article As: K. Legrouri, E. Khouya, H. Hannache, M. El Hartti, M. Ezzine and R. Naslain. Activated carbon from molasses efficiency for Cr(VI), Pb(II) and Cu(II) adsorption: A mechanistic study. Chemistry International 3(3) (2017) 301-310.

INTRODUCTION

The increasing use of heavy metals in industrial activities has caused contamination of natural waters. For example, chromium, lead, cadmium and copper are found in wastewater effluents of industries such as electroplating, plastic and paint manufacturing, mining, metallurgical process, petrochemical process, batteries, paper and pulp (Oboh et al., 2009; Iqbal, and Edyvean, 2004; Bennett et al.,

2001; Iqbal, 2007; Kim et al., 2003; Roque-Malherbe et al., 2007).

At least 20 metals are classified as toxic and half of them are released into the environment in large quantities leading to risks for human health (Iqbal et al., 2005; Kortenkamp et al., 1996). The hexavalent chromium is considered among the very toxic compounds and may cause lung cancer. While Cr(III) is relatively innocuous and immobile, Cr(VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being

absorbed through the skin (Kortenkamp et al., 1996; Demirbas, 2004; Wu, 2008; El Harti, 2013ab). Lead is toxic to living organisms and can bioaccumulate and enter the food chain when released into the environment. It is known to cause mental retardation, reduces haemoglobin production, necessary for oxygen transport, and interferes with normal cellular metabolism, which causes damaging effects on body nervous system (Barbooti et al. 2015; El Harti, 2013; Momčilović et al., 2011; Hassan et al., 2014; Li et al. 2010; Acharya et al., 2009; Swiatkowski et al. 2004). Excess copper is known to be highly toxic to sweet potato, with concentrations as low as 5 μM in the root zone being sufficient to cause significant growth reduction (Roque-Malherbe et al. 2007). At concentrations above 20 μM , prevention root growth and death of the transplanted cutting may result (El Harti, 2013a; Mahmood et al. 2015).

Conventional methods for removing metals from industrial effluents include chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation (Gürel et al. 2005), ion - exchange (Roque-Malherbe et al. 2007; Barbooti, 2010; Gaikwad et al., 2010) and adsorption on different materials (El Harti et al., 2013ab; Al-Jlil, 2009).

The idea of using various agricultural products and by-products for the removal of heavy metals from aqueous solutions has been investigated by several researchers (Bouchelta et al., 2008; Chowdhury et al., 2012; Billy et al., 2013; Ahmedna et al., 2000; Hassan et al., 2013). The efficiency of different organic waste materials as sorbents for heavy metals has been proven, with the obvious advantage of their lower cost compared to other materials (Carrott et al., 2007; Wu et al., 2008; Giwa et al., 2013). Activated carbon appears to be particularly competitive and effective for the removal of heavy metals at trace quantities (Acharya et al. 2009; Li et al., 2010; Hassan et al., 2014; Momčilović et al., 2011).

The aim of this work is to test the removal of heavy metal ions, such as Cr(VI), Pb(II) and Cu(II), by activated carbon prepared from molasses, which are the secondary products of the sugar industry. The importance of this study is ducted by the abundance of this by-product and the important results obtained previously on the activation of molasses by sulfuric acid (K. Legrouri et al., 2001; K. Legrouri et al., 2005; K. Legrouri et al., 2012). The activating agent used in this study was phosphoric acid, which is known by its catalytic properties, and the conditioning variables examined were temperature and heating time. The properties of the activated carbon thus prepared were examined by determination of the maximal adsorption capacity of methylene blue and iodine, BET surface area measurement and scanning electron microscopy observation. The adsorption tests on the three ions, Cu(II), Pb(II) and Cr(VI), were affected by the best material obtained in this study.

MATERIAL AND METHODS

Reagents and chemicals

All chemicals were of analytical reagent grade and no further purification was required. Double-distilled water was used for dilution purpose. The element standard solutions for calibration were prepared by diluting a stock solution of 1000 mg.L^{-1} .

Methods

The elemental analyses were carried out by a GBC 908 PBMT atomic absorption spectrophotometer. All measurements were carried out in an air/acetylene flame.

Specific surface areas of the solid materials were measured by the BET method (Brunauer et al., 1938). The samples were degassed at 160°C for 24 h. A pH-metre Mini 80 (Tacussel, France), equipped with a combined glass electrode and a graduated burette of 0.05 mL, was used.

The surface image of both activated adsorbent was taken with a JED JSM-840 ALGS analytical scanning electron microscope (SEM).

Heavy metal ion solutions

The working stock solutions (1000 mg.L^{-1}) of Cu(II), Pb(II) and Cr(VI) were prepared by dissolving an exact amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled water and further diluted as required. The pH values were adjusted by dropwise addition of concentrated HNO_3 .

Preparation of activated carbon [MP2 (500)]

The precursor used to prepare the activated carbon is molasses and the activation was completed by activation by phosphoric acid. The choice of the precursor and its processing were dictated by two reasons: the molasses is composed essentially by organic matter (more than 90% after dehydration) and the chemical activation by phosphoric acid presents several advantages, amongst which are of lower temperature, shorter time of activation, and higher yield of activated carbon compared to physical activation (Bouchelta et al., 2008).

The weight ratio of the mixture of molasses and phosphoric acid (80%) was of $\text{H}_3\text{PO}_4/\text{precursor} = 2$. After pre-processing at 120°C in an oven for two hours, the mixture was heated in a furnace at 500°C under air. The choice of the activating agent and the weight ratio was based on previous studies by the authors (Legrouri et al. 2001; Legrouri et al., 2005). The thermally treated product, referred to as MP2(500), was washed with distilled water in a Soxhlet extractor, to eliminate excess acid and soluble matter, then dried at 110°C. Before use in adsorption tests, the adsorbent was sieved and more than 95% of the final particles had an average diameter of 100 μm . The performance of MP2(500) activated carbon was evaluated by determination of the maximal adsorption capacity for methylene blue and iodine, the specific surface area (S_{BET}), the surface functions and the morphology by scanning electron microscopy.

Properties of [MP2(500)]

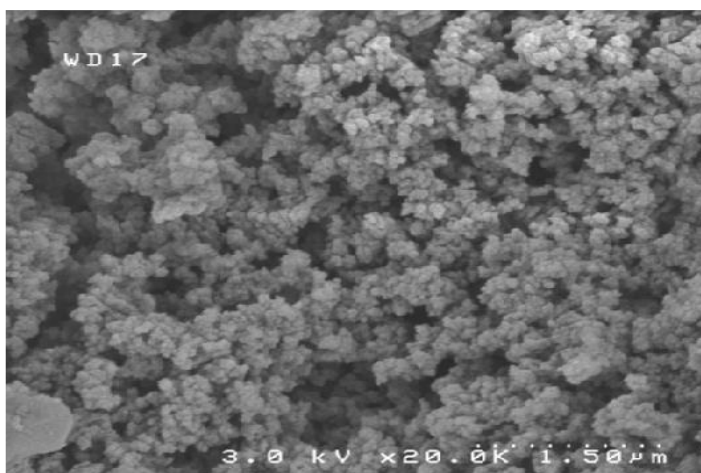


Fig. 1: Scanning electron micrograph of MP2 (500)

The specific surface area (S_{BET}), the total surface acidity and the Electron Microprobe Analysis (EMPA) data for MP2(500) are presented in Tables 1 and 2. The parameters of the adsorption isotherm for methylene blue (MB) and iodine are given in Table 3.

The results mentioned in Tables 1, 2 and 3 show an improvement of textural and structural properties of MP2(500). The values in Table 2 reveal the important rate of carbon and oxygen due to carbonization of the precursor and the formation of the carbon skeleton. The presence of phosphorus suggests the incorporation of this element in the structure of the adsorbent and the formation of C-O-P bonds (Guo et al., 2007; Shrestha Rajeshwar et al. 2012). The value of the specific surface area of the activated carbon exceed $1470 \text{ m}^2/\text{g}$ (Table 1) and the maximum adsorption capacity is higher than 600 mg/g for MB and 1600 mg/g for iodine (Table 3). Besides, the development of the functional surface groups and total acidity is observed (Table 1).

The microtexture observation of MP2(500) by SEM (Figure 1) shows significant morphology differences among the samples. The development of porosity accounts for the values obtained in adsorption tests and specific surface area values.

Effect of pH on adsorption

The effect of initial pH on metal ion adsorption was studied by using 100 mL of a 10 mg/L aqueous solution of either

Table 1: Summary of characteristics values of the prepared activated carbon MP2(500)

Functional groups in surface (meq/g)		
Carboxylic	Lactone	Hydroxyl
0.85	0.10	0.78
Total surface acidity (meq/g)	Total surface basic (meq/g)	S_{BET} (m^2g^{-1})
1.73	0.32	1477

Cu(II), Pb(II) or Cr(VI) and 15 mg of activated carbon. The mixture was stirred at the constant rate of 150 rpm in a temperature controlled orbital shaker maintained at 30°C . The initial pH (pH_0) of the adsorbate solution was adjusted using 1 N HNO_3 or 1 N NaOH aqueous solution without any further adjustment during the sorption process. The mixtures were withdrawn at the end of predetermined time values, t , their contents centrifuged, using a research centrifuge at 5000 rpm for 5 min, and the supernatant liquid was diluted, if required, with double distilled water and analysed for residual metal ions using atomic absorption spectrophotometry. The quantity of removed metal ions (removal percentage) was calculated using relation shown in Eq. 1.

$$R(\%) = \left[\frac{(C_0 - C_f)}{C_0} \right] \cdot 100 \quad (1)$$

Where, R is metal ions recovery (%), C_0 and C_f (mg/L) are initial (t_0) and final (t_f) concentrations of metal ions, respectively.

Adsorption kinetics

The two important physicochemical aspects for the evaluation of the sorption process, as a unit operation, are the kinetics and the equilibrium time of sorption. For kinetics studies, 100 mg/L of adsorbent was added to 500 mL of

Table 2: The electron microprobe values of activated carbon MP2(500)

The electron microprobe values (% atomic)				
C	O	Si	P	Cu
87.37	6.73	0.67	2.89	2.36

aqueous solutions containing 25 mg/L of Cu(II) or 23.4 mg/L of Pb(II) or 24.3 mg/L of Cr(VI). After adjustment of the pH to the desired value, the mixture was shaken at room temperature. The adsorption kinetics was followed for 6 h and it was observed that after 15 min of contact time, the rate of removal of the adsorbate from the solution was gradual and very slow. The present removal of a metal ion at time t_i was calculated using relation shown in Eq. 2.

$$R_i(\%) = \left[\frac{(C_0 - C_i)}{C_0} \right] \cdot 100 \quad (2)$$

Where, R_i is metal ions recovery at t_i , C_0 and C_i (mg/L) are the liquid phase concentrations of metal ions at initial moment (t_0) and time (t_i), respectively

RESULTS AND DISCUSSION

Effect of solution pH

The pH of the solution is an important factor in determining the rate of surface reactions (Carrott P. J. M, and Ribeiro Carrott M. M. L., 2007). Figure 2 shows the influence of the initial pH values of Cu^{2+} , Pb^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ solutions on their

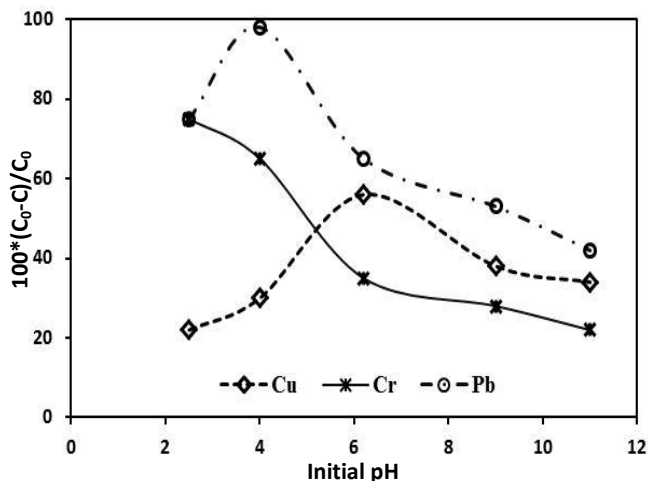


Fig. 2: The starting solution pH influence on the adsorption by MP2 (500) of Cu^{2+} , Pb^{2+} and $\text{Cr}_2\text{O}_7^{2-}$

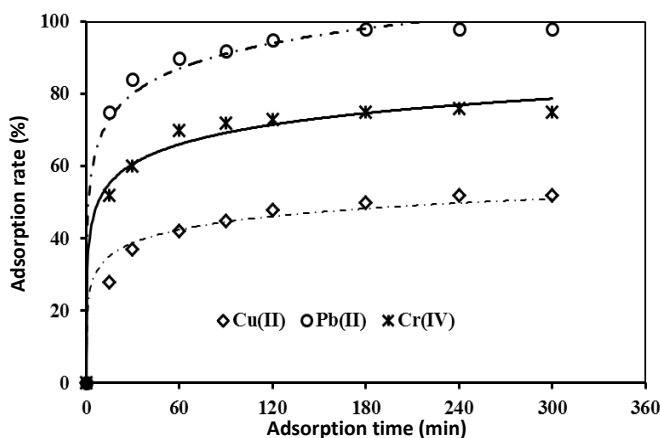


Fig. 3: Kinetics adsorption of Cu^{2+} , Pb^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ on MP2 (500) (Conditions: C_0 (Cu) = 25 mg/L; C_0 (Pb) = 23.4 mg/L; C_0 ($\text{Cr}_2\text{O}_7^{2-}$) = 24.3 mg/L, pH = 6.2, pH = 3.8, pH = 1.8)

adsorption by MP2(500). The first observation is that the adsorption of the three heavy metal ions is strongly controlled by the pH values of the starting solution. The sorption of Cu^{2+} increases with increasing pH. The maximum adsorption (58%) was reached at pH 6.3 indicating the important effect of the solution pH on the adsorption of this ion. The sorption of Pb^{2+} is very important at pH 4, with an adsorption rate close to 100%. For the dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$), the adsorption is favoured at low pH values and becomes more important at pH 2.

Cu^{2+} and Pb^{2+} (effect of pH)

At pH values lower than 3, there is excessive protonation of the carbon surface resulting in a decrease in the adsorption of Pb^{2+} and Cu^{2+} (M^{2+}) (Ghaedi M. and Mosallanejad N. 2013, Saifuddin M. Nomanbhay and Kumaran P. 2005). On increasing the pH of M^{2+} solutions from 3, the percentage removal increased and become quantitative over the pH range 3-6. It is known that divalent metal ions (M^{2+}) can be present in water at different forms such as M^{2+} , $\text{M}(\text{OH})^{+1}$, $\text{M}(\text{OH})_2^0$, $\text{M}(\text{OH})_3^{-1}$, etc. (Bryant P. S., Olaniyi I. et al. 2012). At a pH ≤ 3 , the predominant lead and copper species is always M^{2+} and the M^{2+} removal is mainly accomplished by sorption process (Gaikwad R. W. et al., 2010). The increase in metal removal as pH increased can be explained on the basis of a decrease in competition between proton (H^+) and positively charged metal ion at the surface sites, and by decrease in positive charge which results in a lower repulsion of the adsorbing metal ion.

Thus, the fact that more M^{2+} sorption took place at a higher pH could be attributed to a decrease in competition between H^+ and M^{2+} at the same sorption site of MP2(500). Furthermore, the surface of MP2(500) is more negatively charged at a higher pH, which causes a more electrostatic attraction of M^{2+} .

Cr(VI) (effect of pH)

The pH dependence of chromium adsorption can largely be related to the type and ionic state of the functional groups present on the activated carbon MP2(500) and the chromium ions chemistry in solution (Zainul A. Z. et al. 2009). In the pH range of 1- 6, chromium ions coexists in different forms such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ of which HCrO_4^- predominates (Covarrubias C. et al., 2005).

The favorable effect at low pH can be attributed to the neutralization of negative charges on the surface of the adsorbents by excess hydrogen ions, thereby facilitating the diffusion of the hydrogen chromate ion (HCrO_4^-) and its subsequent adsorption, because HCrO_4^- is the dominant anionic form of Cr(VI) between pH 1.0 and 4.0. This ionic form was found to be preferentially adsorbed on the surface of carbon. The negative charges could result from oxygenated functional groups of basic character such as lactone or hydroxyl groups, chemisorbed at the surface of the pores. The possible explanation for higher adsorption in the acidic region is that the $\text{Cr}_2\text{O}_7^{2-}$ ion is oxidized to Cr^{3+} (Karthikeyan et al., 2005).

As the pH of the solution increases, the predominant species are then CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. More adsorption at acidic pH indicates that the lower pH results in an increase in H^+ ions on the adsorbent surface that result in significantly strong electrostatic attraction between positively charged adsorbent surface and chromate ions. Lesser adsorption of Cr(VI) at pH values greater than 6.0 may be due to the dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent, of which OH^- predominates. This is in accordance with earlier studies that reported the removal of Cr(VI) by different adsorbents

(Gardea-Torresdey J. L. et al. 2000, Liu S. X. et al. 2007, Mohan D. and Pittman C. U. 2006, Schneider R.M. et al. 2007).

Adsorption kinetics

In order to evaluate the adsorption characteristics of MP2(500) for Cu^{2+} , Pb^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ ions, the change of their adsorption rate with time has been investigated (Figure 3). The adsorption rate of the three ions on MP2(500) rises rapidly at the initial stage of adsorption reaching about 75%, 52% and 28% for Pb^{2+} , $\text{Cr}_2\text{O}_7^{2-}$ and Cu^{2+} , respectively, after 30 min of contact time (more than 50% of maximum adsorption rate). No appreciable increase in adsorption rates was observed beyond this time and the equilibrium adsorption was essentially reached within 120 min.

Adsorption isotherms

The adsorption isotherm indicates how the quantities of target species are distributed between the liquid and the solid phases when the adsorption process reaches equilibrium. It is employed to establish the maximum capacity of adsorption of metals on adsorbents, which is expressed in term of metal quantity adsorbed per unit of used adsorbent mass (mg/g or mmol/g).

Different amounts of MP2(500) (between 250 and 1000 mg/L) were added to 250 mL aqueous solutions containing 50 mg/L of Cr(VI) or Pb (II) or 70 mg/L of Cu(II). The mixture was stirred for 8 hours in a batch reactor at atmospheric pressure and constant temperature. The pH was maintained around to desired value of each solution by addition of 0.1 M NaOH or 0.1 M HCl. When the equilibrium was reached, the residual concentration of each ion was measured. Figure 4 shows the isotherms of adsorption of the three ions.

The curves can be classified into two categories according to the classification of Giles et al. (1974):

- Adsorption isotherms of the Pb(II) and Cu(II) are concave curves reversed downwards, which can be classified in the L category. This type of isotherm shows a decrease in the active sites as the solute adsorption progresses. This phenomenon occurs when the attractive forces between the adsorbed species are low, which results in a monolayer adsorption of species in an isolated manner;
- The adsorption isotherm of the chromate ion, which is of S type, is characterized by an upwards concavity. The adsorbed species favour the subsequent adsorption of other molecules (cooperative adsorption). This is due to attractions between these species by Van Der Waals forces, which make them grouped into blocks that are bunched together against each other.

The adsorption isotherms of the three ions were well fitted by the Langmuir and Freundlich models (Freundlich, 1906; Treybal, 1968; Ho and McKay, 1998). The linear forms of the Langmuir and Freundlich isotherms are represented by the equations 3 and 4, respectively.

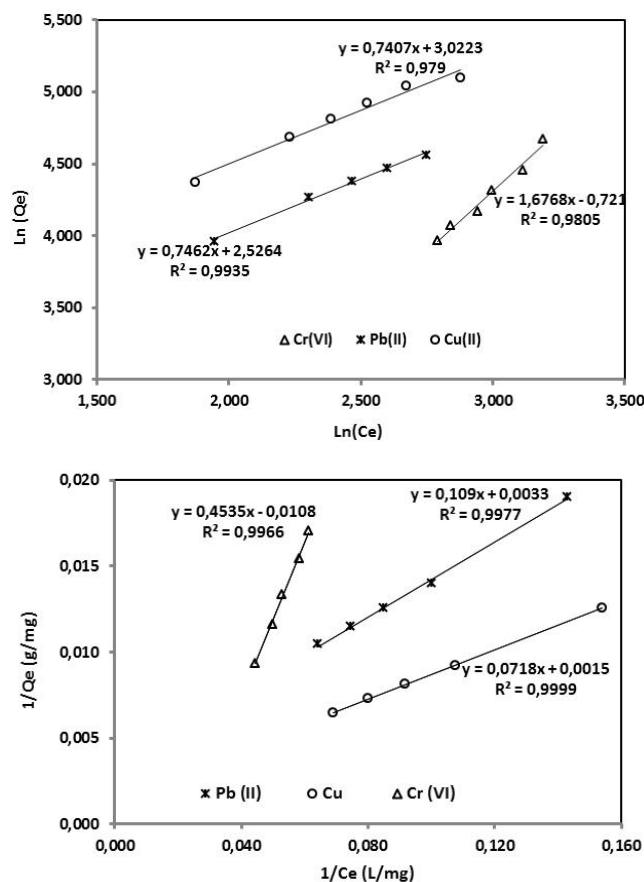


Fig. 5: Langmuir (upper) and Freundlich (lower) Plots of three ions (Cr(VI), P(II) and Cu(II) adsorbed by MP2 (500)

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L Q_m} \right) + \left(\frac{1}{Q_m} \right) C_e \quad (3)$$

Where, K_L = Langmuir equilibrium constant for adsorption (L/mg), Q_m = maximum adsorption capacity (mg/g), Q_e = amount adsorbed at equilibrium (mg/g), C_e = equilibrium concentration (mg/L).

$$\ln q_e = \ln K_F + \frac{1}{n \ln C_e} \quad (4)$$

Where, K_F and n are the isotherm constants of the Freundlich equation.

The isotherm constants of Freundlich and Langmuir were calculated from the plots of C_e/q_e versus C_e and $\ln q_e$ versus $\ln C_e$, respectively (Figure 5), and the results are listed in Table 4.

It is clear that the correlation coefficients (R^2) for the Langmuir isotherm are slightly higher than that for the Freundlich isotherm, which indicates that the uptake occurs on a homogenous surface by monolayer adsorption and can be described in terms of chemisorption (bond formation between adsorbent and adsorbate) (Gregg and Sing, 2000). The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium

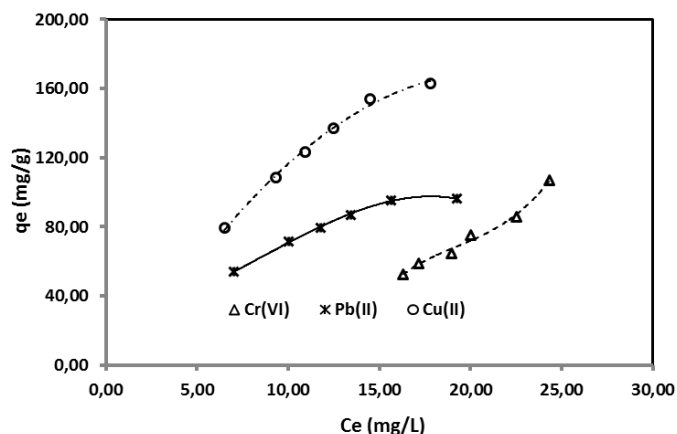


Fig. 4: isotherms of adsorption of the three ions (Cu(II), Cr(VI) and Pb(II)) on (MP2 (500))

The order of adsorption affinity based on the amount of metal ion uptake (mg metal ion/g of activated carbon) is as follows: $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cr}^{6+}$ (Table 4). The values of maximum adsorption capacity by the Langmuir model equal 144.93 mg/g, 303.03 mg/g and 526.32 mg/g for Cr(VI), Pb(II) and Cu(II), respectively. The importance of the values of q_m is attributed to the high surface area of MP2(500), which is more than $1400 \text{ m}^2\cdot\text{g}^{-1}$. The difference of the adsorption capacity between the three metal ions is due to the form, size and electrical charge of the ions. The Cu(II) ion has a spherical form and a too small size compared to those of the Pb(II) ion and the dichromate ion (most dominant ion at pH around 4). Furthermore, the surface functional groups, existing on the surface of the activated carbon, are rich in carbonyl group which promotes the strong attractive interactions between the cations and the active surface of the MP2(500).

Table 3: Summary of isotherm parameters of adsorption of methylene blue (MB) and iodine by MP2(500)

Adsorbate	Langmuir		Freundlich		Elovich	
	$Q^{\circ}(\text{mgg}^{-1})$	b_1	K_f	N	$Q^{\circ}(\text{mgg}^{-1})$	b_2
MB	625	1,45	399	0,166	270	0,198
Iodine	1666	0,285	786	0,166	910	0,028

Table 4: Isotherm parameters obtained for the adsorption of Cr(VI), Pb(II) and Cu(II) ions onto MP2(500)

Metal Ions	Langmuir				Freundlich			
	$q_m(\text{mg/g})$	b_1	R_L	R^2	K_f	N	$1/n$	R^2
Cr(VI)	144.93	0.248	0.544	0.996	2.056	0.596	1.68	0.980
Pb(II)	303.03	0.030	0.398	0.998	12.508	1.340	0.746	0.993
Cu(II)	526.32	0.030	0.340	0.999	20.538	1.350	0.741	0.979

parameter, R_L (Langmuir, 1918; Ferrero, 1907) which is defined by:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

Where, b is the Langmuir constant and C_0 the initial concentration (mg/L). $R_L > 1$ = Unfavorable adsorption, $0 < R_L < 1$ = Favorable adsorption, $R_L = 0$ = Irreversible adsorption, $R_L = 1$ = Linear adsorption, R_L value between 0 and 1 indicated favourable adsorption.

The adsorption of the three ions followed the Langmuir model for the present systems indicated the formation of monolayer coverage of adsorbate at the outer surfaces of the adsorbent. Likewise, it may be stated that the ion retention by MP2(500) was ruled by physisorption as well as a cationic exchange process. It was found that the metal ion uptake by MP2(500) increased with increasing initial metal ion concentrations.

Generally, the mechanisms of heavy metal ion adsorption on activated carbon were very complicated and appear attributable to physical adsorption, electrostatic attraction, precipitation and chemical interaction between the heavy metal ions and the surface functional groups. In our case, two mechanisms are most likely. The first is the intra granular distribution for heavy metal ions of small size which limits the activated carbon adsorption capacity (case of copper ions adsorption). The second is the chemical interaction and the electrostatic attraction between metal ions and the surface functional groups formed by chemical activation of MP2(500). This latter is the major adsorption mechanism in our case (Selomulya et al., 1999; Mohan et al. 2005; Demiral et al., 2008; Mohan and Pittman, 2006; Agarwal et al., 2006). The existence of various surface functional groups, such as basic, phenolic, carboxyl, carbonyl and hydroxyl groups (Meunier et al., 2003 ; Tee and Khan, 1988; Annadurai et al., 2002), on the surface of MP2(500) increased the adsorption amount of the three metal ions. Some suggestive mechanisms

for the adsorption of Cu(II), Pb(II) and Cr(VI) are electrostatic attraction (physical adsorption) and chemical interaction between the heavy metals ions and the surface functional groups of MP2(500). In view of MP2(500) efficiency, it could be used for the remediation pollutant of environmental concern (Akram et al., 2017; Babarinde et al., 2016; Babarinde and Onyiaocha, 2016; Bhatti et al., 2016; Iqbal et al., 2013; Iqbal, 2016; Iqbal et al., 2015; Iqbal and Bhatti, 2015; Iqbal et al., 2016; Iqbal and Nisar, 2015; Iqbal et al., 2017; Jamal et al., 2015; Manzoor et al., 2013; Mushtaq et al., 2016; Nadeem et al., 2016; Nisar et al., 2016; Nouren et al., 2017; Qureshi et al., 2015; Rashid et al., 2016; Sayed, 2015; Shindy, 2016; Shindy et al., 2016; Shoukat et al., 2017; Tahir et al., 2016a; Tahir et al., 2016b; Ullah et al., 2013).

CONCLUSIONS

The experimental results of the adsorption of Cu(II), Cr(VI) and Pb(II) metal ions on the activated carbon (MP2(500)) prepared from molasses are encouraging. The adsorbent may be used for the removal of the metal ions from aqueous solutions. The adsorption tests indicate the affinity of MP2(500) for the ions in the following order $\text{Cu}^{2+} > \text{Cr}^{6+} > \text{Pb}^{2+}$. The adsorption of the three ions is governed by monolayer adsorption given that the correlation coefficient (R^2) of the Langmuir model is close to unity.

ACKNOWLEDGEMENTS

The Authors sincerely appreciate financial support from Hassan II academy of science and technology (2011-2014). Also, Authors appreciated valuable discussion from Prof. Roger Naslain x-director of Thermostructural Composites Laboratory UMR5801 (CNRS-Snecma-UB1-CEA).

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