

Study of the Effect of Various Parameters on the Adsorption of Heavy Metals by Bentonite-Polypyrrole Composite

Ben Bouabdallah, Amina*⁺

Laboratory Food Technology, Faculty of Technology, Process Engineering Department,
M'hamed Bougara University of Boumerdes 35000, ALGERIA

Djelali, Nacer-Eddine

Laboratory Treatment and Formatting of the Polymers (L.T.M.F.P), Faculty of Science, Chemistry Department,
M'hamed Bougara University of Boumerdes 35000, ALGERIA

ABSTRACT: In this research, the adsorption of heavy metals (Chromium and Lead) in aqueous solutions was investigated using a Bentonite-Polypyrrole composite. The composite was synthesized via *in situ* polymerization of pyrrole in the presence of bentonite (40%). Tests were conducted under various conditions to study the influence of different parameters (pH, initial concentration, contact time, competing ions, Zeta potential, organic matter) on the adsorption process. Langmuir and Freundlich's isothermal models were applied to assess the equilibrium data. The kinetics of adsorption were determined using the Lagergren pseudo-second-order model. The characterization of the composite was tested by Scanning Electron Microscopy (SEM), Fourier Transform InfraRed (FT-IR) spectroscopy, and X-Ray Diffraction (XRD), and the results show intercalation of polypyrrole in the bentonite layers. The best results were obtained for a contact time of 60 minutes, an initial concentration of 10 mg/L, pH 2 for chromium, and pH 5 for lead. The presence of humic acids can modify the surface characteristics of the composite and affect the adsorption capacity. The measurements of the electrokinetic potential show that the zeta potential of the composite after adsorption of the metal cations is greater than that of the corresponding composite. The presence of organic matter regularly decreases the maximum exchange capacity with respect to metal cations. The Langmuir and Freundlich isotherm indicated a high affinity of Bentonite-Polypyrrole composite for chromium (VI) and lead (II) ions.

KEYWORDS: Bentonite-Polypyrrole; Adsorption; Heavy metals; Synthesis, Characterization; Isotherm.

INTRODUCTION

The presence of heavy metals in industrial wastewater has posed many serious environmental problems due to their non-biodegradable properties and toxicity, even

at low concentrations [1,2]. In addition, the problem does not cause only degradation of the physicochemical and biological quality of the environment but also generates

* To whom correspondence should be addressed.

+ E-mail: a.ben-bouabdallah@univ-boumerdes.dz

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many waterborne diseases [3]. These heavy metal ions are found in various industry sources such as electroplating, textile, metal finishing, chemical manufacturing and storage batteries [4].

The most common treatment methods are precipitation, membrane processes, electrolytic recovery, liquid-liquid extraction and sorption (adsorption, ion exchange) [5,6]. Among these processes, adsorption is one of the most efficient techniques owing to its various advantages such as high relatively easy regeneration, adsorption capacity, fast kinetics, and the use of a large variety of adsorbent materials [7,8].

Adsorption is generally described by the study of isotherms [9]. Of many mathematical models making it possible to represent isotherms have been developed. The most used models are the Langmuir and Freundlich models because their mathematical expressions are simple and make it possible to correctly represent the equilibrium adsorption isotherms in the aqueous phase in the majority of cases [10,11].

The adsorption in batch mode can depend on several parameters such as pH, temperature, amount of adsorbent, contact time, and speed of agitation [12]. Other parameters can influence the adsorption phenomenon such as: the variation of the electrokinetic potential (zeta potential), the presence of competitive ions, and organic matter.

Zeta Potential (ZP) is a parameter that expresses the electrochemical equilibrium between particles and liquids like in nanoparticle colloidal solutions with applications in medicine, pharmaceuticals, chemical production, mineral processing, and water and soil purification. [13]. This potential has a maximum value at the surface of the particle and decreases with the distance from the surface, this decrease is affected by the characteristics of the diffuse layer, as well as by the number and type of ions in the charged solution [14]. The ZP makes it possible to characterize the electric charge of the surface of the particle as a function of its environment [15]. It also measures the importance of repulsion or attraction between particles, giving a detailed description of the dispersion mechanism thus allowing the control of electrostatic dispersion. The higher this potential, the greater the repulsive forces between the particles, which leads in practice to a dispersion of the particles. On the contrary, when the potential approaches neutrality, the forces of attraction will be predominant over the forces of repulsion. The electrical charge of a particle depends

on the pH, ionic strength, composition of the electrolyte, and the dielectric constancy of the solution [16,17]. When the charge of the particles is zero, the electrostatic interactions are zero and the charge should no longer depend on the ionic strength. The isoelectric point (IEP) or point of zero charge or PZC (Point of Zero Charge), is defined as being the pH of the aqueous solution in which the solid exists under a zero electric potential called pH_{PZC} . If the pH of the solution is higher than pH_{PZC} , the surface is negative, it becomes positive for values lower than pH_{PZC} [18,19].

The presence of organic matter, especially Humic Acids (HA) and Fulvic Acids (FA) in water, considerably influence the adsorption of heavy metals on the composite used as adsorbent. HA and FA are responsible for the coloring of water, have properties of ion exchangers and properties of complexation [20]. HA has excellent binding properties and electrostatic interactions with heavy metals, leading to metal-organic complexes. These complexes can affect the adsorption of heavy metals on composite adsorbents. Heavy metal adsorption in the presence of HA may depend on several factors, such as the surface charge of the adsorbent type and abundance of functional groups in HA, concentration of HA, etc. [21]. HA are present in all natural waters, which is why we used them as organic ligands to test their influence on this adsorption.

It is known that wastewater contains, in varying concentrations, organic and inorganic ions, mainly cations and anions such as nitrates, chlorides, sulfates, carbonates, and hydrogenocarbonates, etc [22,23]. So to better understand the influence of these ions on the heavy metal retention by the B-Ppy composite, experiments were carried out by adding to each solution, salts such as NaCl and CaCl_2 .

EXPERIMENTAL SECTION

Materials and methods

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and the pyrrole monomer were purchased from Sigma-Aldrich.

The clay we used is a bentonite rich in montmorillonite and coming from the North-West of Algeria. It comes from the Hammam Boughrara deposit (Maghnia).

The zeta potential measurements were carried out at the UR/MPE laboratory (Materials, Processes and Environment Research Unit) at the University of Boumerdes. The zetameter used is of the Malvern (2000) type. It is made up of a unit of measurement, in which the sample is injected,

and a cell where an electric field is applied to move the electrical charges contained in the sample. This unit is controlled by a microcomputer using "zeta sizer Advanced" brand software. The device performs the automatic analysis three times and displays the results as a peak.

Metal salts: potassium bichromates $K_2Cr_2O_7$ and lead nitrates $Pb(NO_3)_2$ are supplied by the chemistry laboratory at the University of Boumerdes. They are very soluble in water.

The mineral salts ($NaCl$ and $CaCl_2$) added as well as the humic acids used are provided by the chemistry laboratory of the University of Boumerdes.

Characterization

The scanning electron microscopy (SEM) images were obtained using a LEO-435 Model SEM (England). All samples were coated with gold prior to analysis.

Fourier-Transform InfraRed FT-IR) spectroscopy (measurements were run on a Magna-850 (Thermo Nicolet, Madison, WI) spectrometer using KBr pellets.

Wide-angle X-Ray diffraction (WAXD) patterns were obtained in transmission mode by using a SIEMENS diffractometer equipped with a 2D wiregrid Hi-Star detector, using a $Cu-K\alpha$ graphite monochromated radiation ($\lambda=0.15418$ nm). Samples were inserted in 0.3 mm special glass capillaries.

Synthesis of B-Ppy composite

The B-Ppy composite was chemically synthesized by the polymerization technique. To obtain a better dispersion, a known mass of bentonite (varies from 0.2 for 20% to 2g for 71.4%) was put in a three-necked flask, then we poured 37.5 mL of distilled water as the medium of synthesis and 0.75 mL of pyrrole taken using a precision pipette. The mixture was stirred for 2 days for better insertion of the monomer inside the bentonite sheets. To the reaction medium obtained, we added with stirring at 23°C and for 15 minutes 7.4 g of ferric chloride ($FeCl_3 \cdot 6H_2O$) dissolved in 12.5 mL of distilled water for the polymerization of pyrrole, the reaction mixture is maintained under moderate agitation for 2 hours. The product obtained is filtered and then washed with distilled water and acetone. It is then dried at 95 °C in an oven until obtaining a fine black powder. Finally, the synthesized composite is stored in a desiccator, ready for use.

Study of the adsorption of metal cations on the B-Ppy composite

To evaluate the adsorption capacity, the synthesized B-Ppy composite obtained was applied as an adsorbent for the decontamination of chromium Cr (VI) and lead Pb (II) ions from polluted aqueous solutions. The effect of different parameters on the adsorption process such as zeta potential, competitive ions and organic matter are studied. The adsorption experiments were carried out by the batch technique.

Adsorption isotherms

Adsorption isotherms are performed in order to assess the adsorption capacity of the composite. The adsorption isotherm is fundamentally important in designating the types of adsorption [24]. Equilibrium adsorption studies give the equilibrium adsorption capacity which is often described in terms of the Freundlich adsorption isothermal equation, or the equally well known Langmuir equation. These two equations are characterized by certain constants whose values express the surface properties as well as the affinity of the solid composite, for the species to be adsorbed.

Adsorption kinetics

The kinetics of adsorption of Cr (VI) and lead (II) onto B-Ppy were determined using the Lagergren pseudo-second order model. The linearized form of the pseudo-second order is given by equation 1.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (1)$$

Where k_2 (g/mg/min) are the pseudo-second order rate constant, q_t is the amount of metal cation adsorbed at any time (mg/g) and q_e is equilibrium adsorption capacity (mg/g).

RESULTS AND DISCUSSION

Effect of the bentonite charge fixed in the B-Ppy composite on the adsorption of metal cations

To study the effect of the mass of bentonite added in the synthesis of the B-Ppy composite, we varied the percentage of bentonite from 20 to 71.4%, to determine the optimal mass of bentonite fixed in the composite for better adsorption of metal cations. The results are shown in Fig.1 and Fig. 2.

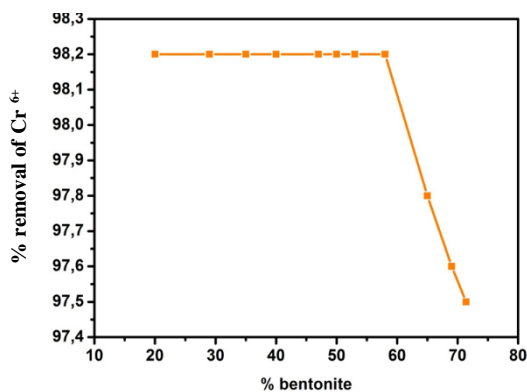


Fig. 1: Effect of bentonite load on chromium adsorption.

The graphs show that the percentage of metal cation removal is almost constant up to 60% of bentonite added during the synthesis of the B-Ppy composite, then decreased with a further increase in% of bentonite using a concentration of 10mg / L for the two metals at pH = 2 for chromium and pH = 5 for lead.

The decrease in the efficiency of the composite may be due to the increase in the amount of bound bentonite, since other bentonite platelets may not have been fully exfoliated, therefore limiting the exposure of other sites of bentonite available for adsorption of metal ions and also, the lowest% amount of intercalated Ppy that is involved for adsorption. Indeed, we chose a B-Ppy composite containing 40% bentonite as a model composite for all the experiments.

Study of the effect of various parameters on chromium adsorption Cr(VI)

Effect of initial concentration

For this study, the initial concentration of chromium (VI) was varied in the range of 1 to 20 mg/L, and the results are shown in Fig.3.

We found that the adsorption capacity increases from 2 to 2.5 mg/g when the initial concentration of Cr(VI) increases from 1 to 10. Beyond this latter concentration, the amount of Cr(VI) adsorbed per one gram of carrier increases only slightly as the initial concentration increases by 10 to 20 mg/L. The reduction in the quantity of Cr(VI) adsorbed is probably due to the increase in the number of chromium ions in the solution for the same number of sites and the same adsorbent surface. The increase in the quantity of Cr(VI) adsorbed per unit mass of composite is the result of the occupation of the surface and of the free sites,

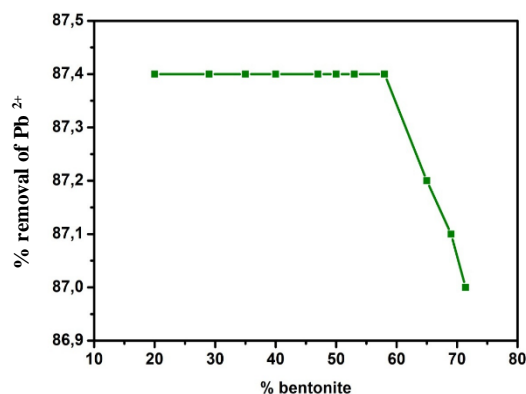


Fig. 2: Effect of bentonite load on lead adsorption.

inaccessible to low concentrations of Cr(VI) in the solution. The same variations were observed by Vaddi, D.R. *et al.* for the adsorption of chromium by Groundnut Shell Activated Carbon@Al Embedded Material [25]. Therefore, the initial Cr(VI) concentration is set at around 10 mg/L to allow for optimal adsorption.

Effect of pH

pH is varied from 1 to 10 and adjusted by adding NaOH soda or hydrochloric acid HCl. The results are shown in Fig.4.

From this graph we noticed that the ultimate adsorption capacity is obtained at pH=2, this is probably due to the reduction of hexavalent chromium (VI) to trivalent chromium Cr(III) [3], after this point, we noticed a decrease in retention capacity with increasing pH, this behavior can be explained as follows: The predominant species of Cr(VI) in aqueous solutions in the pH range of 2 to 6 are monovalent dichromates (HCrO_4^-) and divalent ($\text{Cr}_2\text{O}_7^{2-}$), at pH > 6 the dominant species is chromate (CrO_4^{2-}), so at low pH the H^+ ions which increase the affinity for the negatively charged HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ anions to attach to the composite without competition for adsorption sites. When the pH increases, OH^- ions are present in the solution in competition with chromate ions (CrO_4^{2-}) which decreases the adsorption capacity in this pH range. Indeed, the optimal pH is set at 2. Similar results have been found in other studies [26, 27].

Effect of contact time

The contact time is varied from 5 to 180 min and the results are shown in Fig.5.

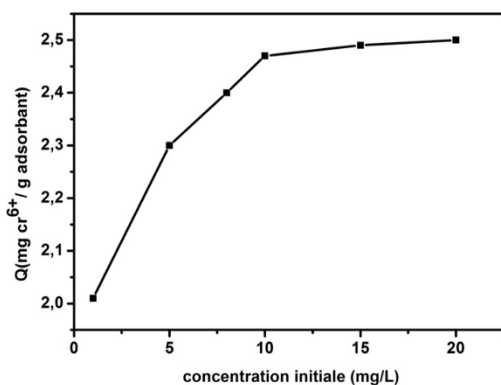


Fig. 3: The influence of the initial concentration on the adsorption of chromium by B-Ppy composite.

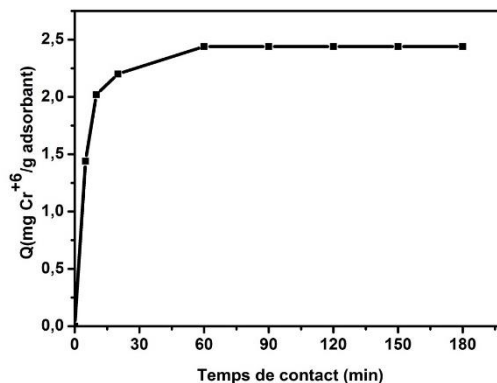


Fig. 5: The effect of contact time on the adsorption of chromium by B-Ppy composite.

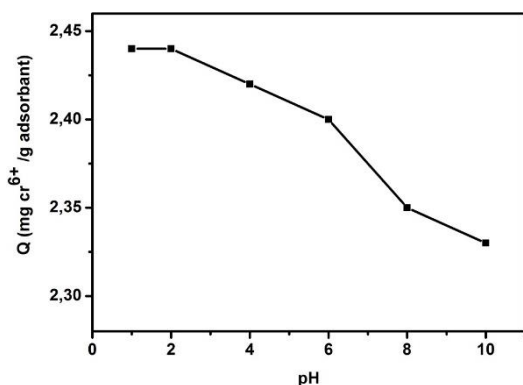


Fig. 4: Effect of pH on the adsorption of chromium by B-Ppy composite.

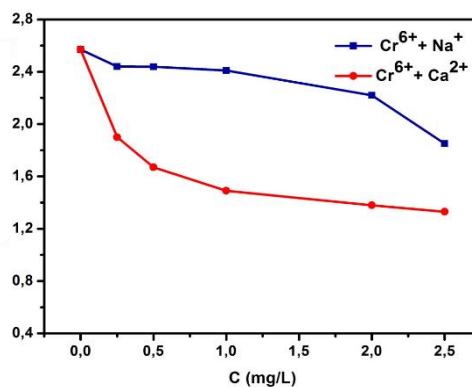


Fig. 6: Influence of the concentration of NaCl and CaCl₂ on the adsorption of chromium by B-Ppy composite.

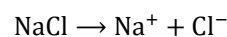
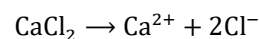
We have noticed that this curve has the appearance of saturation curves which can be divided into two phases: The first is short and fast, while the second is of medium speed until reaching the saturation level at 60 min. This type of two-phase adsorption is also observed in other studies [26, 28]. The rapidity of the first phase is due to the availability of active sites, as these are saturated with time by chromium ions, we found a low adsorption capacity and the adsorption phase is slow. Therefore, the optimum contact time for the elimination of chromium (VI) by the B-Ppy composite is set at 60min. The same result was obtained by Panda H et al [29].

Effect of competitive ions

The presence of the competitive ions, Na⁺ and Ca²⁺ in the metal solution can influence the adsorption of Cr (VI) on the B-Ppy composite. The effect of different concentrations

of NaCl and CaCl₂ on chromium adsorption is shown in Fig.6.

The addition of CaCl₂ and NaCl to the metal solution causes these solutes to dissolve according to the following reactions:



The medium becomes enriched in Ca²⁺ and Na⁺ ions, which causes a decrease in the amount of adsorption of metal cations. This is due to the competition between the common Na⁺ and Ca²⁺ ions and the chromium ions for attachment to the composite. It is also noted that the affinity of the composite is greater for sodium than for calcium due to the high ionic strength of Ca²⁺ which prevents the activity of Cr (VI) ions. The Results were comparable to those of other adsorbents reported in the literature [30, 31].

Table 1: Effect of humic acids on the adsorption of chromium by the B-Ppy composite.

Adsorbent	Adsorption capacity (mg/g)	
	Cr ⁶⁺	Cr ⁶⁺ + Humic acid
B-Ppy composite	2.54	1.9

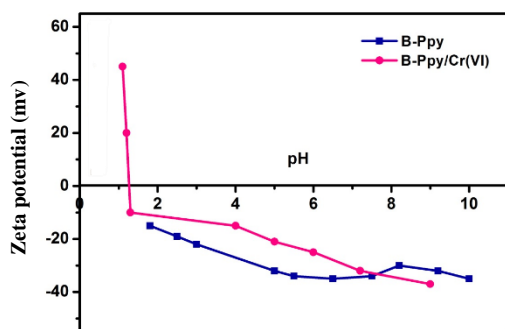


Fig. 7: Comparative study of the variations of the zeta potential of the composite before and after adsorption of chromium.

Effect of variation of electrokinetic potential (Zeta potential)

The description of the adsorption of ions requires knowledge of the nature and number of electric charges carried by the adsorbent surfaces, and of their variations depending on the ionic composition of the medium, the pH in particular, characterized by points of zero electric charge. It also requires a representation of the distribution of electric charges at the liquid/solid interface. The variation of the zeta potential as a function of the pH of the composite before and after the adsorption of chromium (VI) is shown in Fig. 7.

It is observed that the zeta potential is canceled respectively for the composite alone and the composite after fixing of the chromium around pH: 1 and 1.3, which can confirm the occupation of certain sites by the positive charges of Cr⁶⁺. In the case where the isoelectric point (point of zero charge ZPC) takes the greatest value, that is to say in the case of a composite comprising chromium [32]. These results indicate that the B-Ppy composite had a strong affinity for positively charged chromium.

Effect of organic matter

The competitiveness of chromium ions in the presence of organic matter was also tested with humic acids. The presence of HA increases the quantity of metal retained by

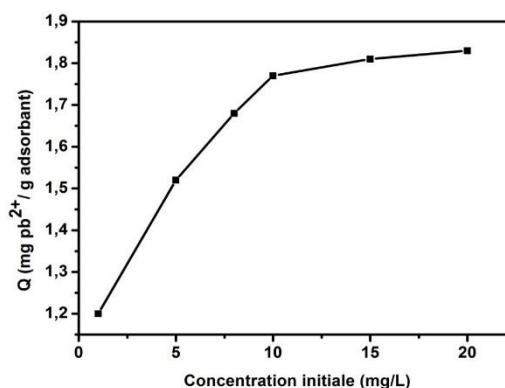


Fig. 8: The influence of the initial concentration on the adsorption of lead by B-Ppy composite.

the adsorbent, the HA acids keep ions in solution and prevent them from precipitating in the form of metal hydroxides, thus promoting their contact with the composite in suspension and therefore their retention by the latter. However, the results we obtained show that the fixing capacity of chromium is reduced in the presence of HA. These results would be due to a strong affinity between the composite and HA which, at high concentrations, could more or less saturate the composite surface, and thus mask the adsorption sites [33]. The results of the adsorption capacity of chromium on the composite in the absence and presence of HA are given in Table 1.

Study of the effect of various parameters on lead adsorption Pb(II)

Effect of initial concentration

The influence of the initial lead concentration on the adsorption process is shown in Fig.8.

The adsorption curve obtained shows a fairly rapid increase in the retention capacity (in mg/g) in the low concentration zone. The adsorption capacity continues to increase with the rise in the initial concentration indicating that strong interactions take place between the exchange surface and the pb²⁺ cations [34]. Then, a decrease in the adsorption capacity is observed at C₀>10 mg/L which may be due to the saturation of the active sites on the surface

of the adsorbent. These results are similar to those obtained previously for chromium.

Effect of pH

The results relating to the study of the effect of pH on the adsorption of lead on the B-Ppy composite are represented in Fig.9.

The results show that the adsorption capacity increases with increasing pH until reaching an optimal adsorption capacity at pH = 5, at very acidic pH we noticed that the adsorption is not as important, this is due to the positive charge dominating the surface of the adsorbent, thus a noticeably high electrostatic repulsion exists between the positive charges of the adsorbent surface caused by the H⁺ protons and the positive charges of lead. These results agree with those obtained by *Matthews T et al.* [35]. Between pH 4 and 7 there is an increase in the adsorption capacity which can be explained by the dissociation of the active sites on the surface of the adsorbent and which become negatively charged which causes the attraction of the positively charged lead in the solution. At pH greater than 7, a decrease in the adsorption capacity is observed due to the precipitation of cadmium in the form of hydroxides.

Effect of contact time

The influence of the contact time on the lead adsorption process on the B-Ppy composite is shown in Fig.10.

From this graph we observed a strong increase in the lead elimination capacity of the composite during the first minutes of contact between the solution and the composite, followed by a slower evolution until the equilibrium is reached at 60 min. The rapid adsorption is due to the availability of active sites for metal ion binding. The slowing down of adsorption after the equilibrium time can be explained by the phenomenon of diffusion of lead ions in the pores of the composite. These results agree with those obtained previously by other studies [34, 36].

Effect of competitive ions

In this study, the mass of the composite is fixed at 0.2g, the volume of the metal solution at 50mL, the pH at 5, and the common ions used are Ca²⁺ and Na⁺. To study the effect of the latter on lead adsorption, we varied the concentration of CaCl₂ and NaCl added to the reaction medium (from 0.1 to 2.5 mg / L). The results obtained are shown in Fig.11.

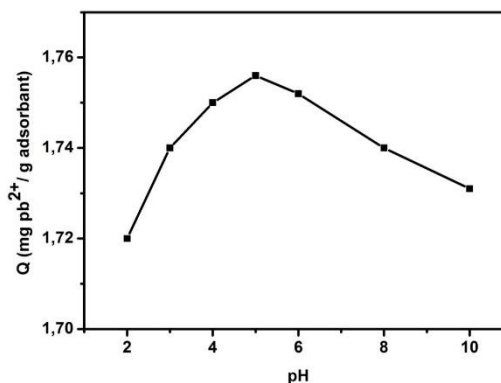


Fig. 9: Effect of pH on the adsorption of lead by B-Ppy composite.

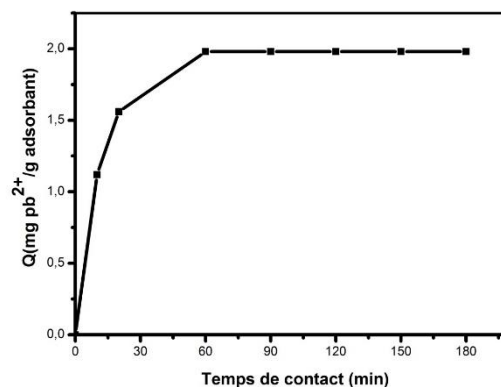


Fig. 10: The effect of contact time on the adsorption of lead by B-Ppy composite.

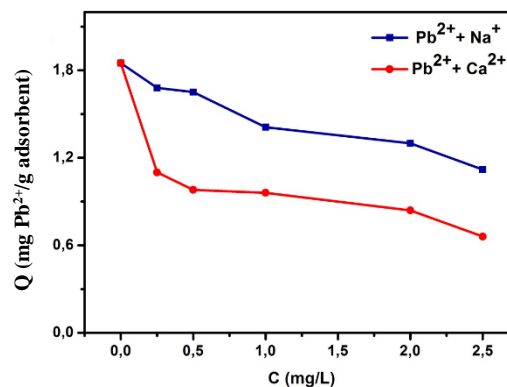


Fig. 11: Influence of the concentration of NaCl and CaCl₂ on the adsorption of lead by B-Ppy composite.

At equilibrium, the amount of adsorption of lead ions by the composite depended on the ionic strength.

This phenomenon can be explained by two factors. First, the metal ion forms complexes with the sites of the composite, which promote adsorption when the concentration of the competing salt is lowered. This could indicate that the adsorption between the functional groups of the adsorbent and the metal cation interacted mainly ionic in nature, which is consistent with an ion exchange mechanism. The second factor is the influence of high ionic strength on the activity coefficient of lead ions, which limits their transfer to the solid surface [37]. Since CaCl_2 solution has more ionic strength than NaCl solution at the same concentration, it has a great influence on the adsorption amount. These results also showed that competitive adsorption is the main reason for the decrease in adsorption capacity.

Effect of variation of electrokinetic potential (Zeta potential)

To determine the electrokinetic potential, particles in a dilute suspension is set in motion under the effect of an electric field. The measurement of their speed and direction makes it possible to calculate the zeta potential associated with them. We represent in Fig. 12 the change in zeta potential as a function of pH for the composite before and after the adsorption of lead.

From the results, we found that the pH of the isoelectric point or pH of the point of zero charge is higher than the pH of the solution. The surface of the composite is therefore negatively charged, which promotes electrostatic attractions between the positively charged metal cation and the active sites of the composite and allow the retention of lead [38].

Effect of organic matter

Humic Acid (HA) has ion exchange properties and complexing properties thanks to its numerous functional groups $-\text{COOH}$ and $-\text{OH}$ [39].

In the presence of HA, the adsorption capacity of lead is considerably reduced (Table 2). The reason is that this metal forms a complex with HA in solution, so it is not adsorbed to the composite surface. Thus a part of HA can attach to the composite surface which causes a reduction in the adsorption capacity. Similar results were observed by Luyao W. *et al.* [40] who found that also adding fulvic acid to the solution containing metal ions Pb, Cu and Cd prevented the adsorption of these cations on the clay.

Table 2: Effect of humic acids on the adsorption of lead by the B-Ppy composite

Adsorbent	Adsorption capacity (mg/g)	
	Pb^{2+}	Pb^{2+} + Humic acid
B-Ppy composite	2	1.43

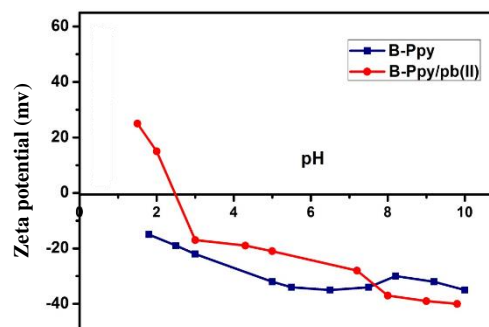


Fig. 12: Comparative study of the variations of the zeta potential of the composite before and after adsorption of lead by the B-Ppy composite

Adsorption isotherms

The exploitation of the results according to the laws of Freundlich and Langmuir is carried out by considering a fixed initial concentration (10 mg / L) in metal cations (chromium and lead) and variable doses of composite. The linear shapes of these isotherms are shown in Fig. 13, Fig. 14, Fig 15, and Fig. 16.

The values of the parameters of the Langmuir and Freundlich isotherms for chromium and lead are grouped together in Table 3.

According to Table 3, we can notice that the correlation coefficients R^2 exceed 0.98 which shows that the experimental results coincide perfectly with the linear form of the two models. For the Freundlich isotherm, we notice that the value of n is greater than unity, which indicates favorable adsorption.

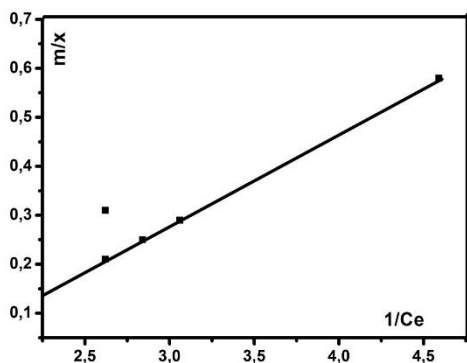
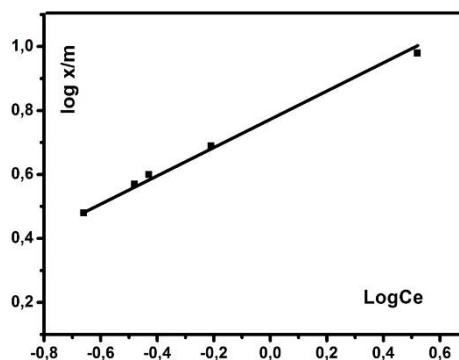
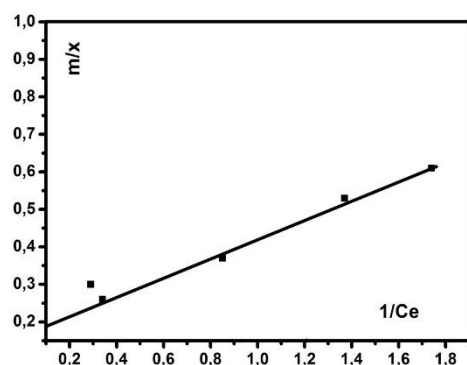
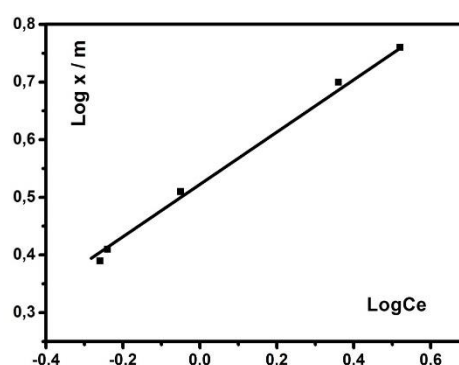
The R values obtained indicate that the process of adsorption of Cr (VI) and Pb (II) by the composite is efficient. These results agree with those obtained with previous work [41, 42].

Adsorption kinetics

Linear plots of t/q_t versus t (Eq. (1)) are shown in Fig. 17 and k and q_e values, obtained from the slopes and intercepts, are presented in Table 4.

Table 3: Adsorption kinetics model parameters for chromium (VI) and lead (II) adsorption.

Adsorbent B-Ppy	Langmuir isotherm			Freundlich isotherm		
	q_m	b	R%	K	n	R%
Cr(VI)	7.14	5.55	99.86	6.12	2.08	98.54
Pb(II)	5.26	4	99.25	3.32	2.27	98.25

**Fig. 13: Langmuir isotherm for chromium.****Fig. 15: Freundlich isotherm for chromium.****Fig. 14: Langmuir isotherm for lead.****Fig. 16: Freundlich isotherm for lead.**

Characterization of the Bentonite-Polypyrrole composite XRD analysis

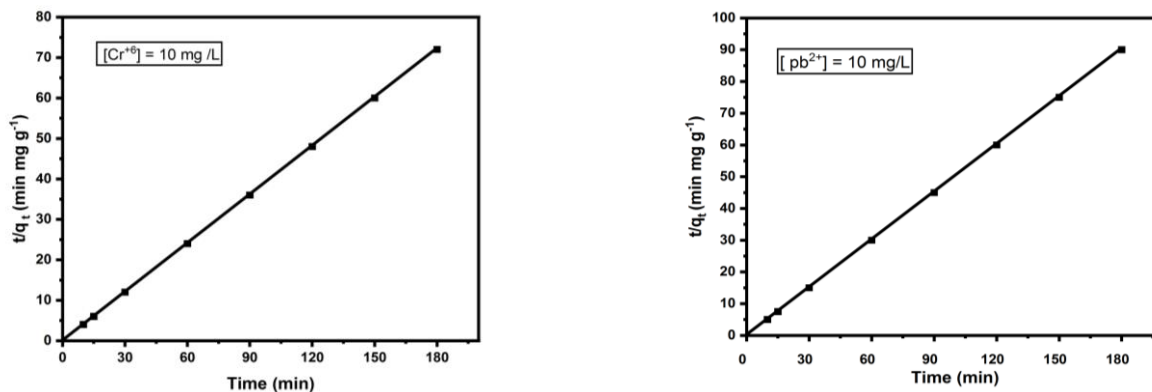
Fig. 18 shows the X-ray diffraction pattern of bentonite, Ppy and B-Ppy composite. The X-ray diffraction pattern of pure Ppy shows broad amorphous diffraction at about $2\theta = 15^\circ$ - 35° . This broad peak, centered around 26° , is characteristic of amorphous Ppy and are due to the scattering from Ppy chains at the interplanar spacing [43].

The XRD diagram of the bentonite showed crystal peaks at 7.6° , 22.10° , 29.97° , 36.55° and 40.34° which correspond respectively to Montmorillonite (001), Quartz (402), Montmorillonite (005), Quartz (111) and Quartz (200), these peaks are seen in the composite but it is observed that the crystalline peaks of the montmorillonite at $2\theta = 7.6^\circ$ and $2\theta = 29.97^\circ$

move towards lower angles for the B-Ppy composite, which corresponds to an increasing distance between the planes of the atoms, this is a consequence of the intercalation process of Ppy chains in between the clay layers. The success of the intercalation is mainly verified by measuring the reticular distance of the (001) and (005) planes of the Montmorillonite structure, which was calculated using Bragg's law. The reticular distance changes from 13.4 \AA ($2\theta = 7.6^\circ$) and 2.99 \AA ($2\theta = 29.97^\circ$) in bentonite to 15.5 \AA ($2\theta = 7.4^\circ$) and 3.19 \AA ($2\theta = 28.3^\circ$) in the B-Ppy composite respectively. This increase is due to intercalation of the polypyrrole into the bentonite layers. These results are also in good agreement with the previously demonstrated synthesis of Poly(p-phenylenediamine)/Montmorillonite Composites [44].

Table 4: Pseudo-second order rate constants for the removal of chromium (VI) and lead (II) by B-Ppy composite.

Metal	C_0 mg/L	k_2	q_e	R^2
Cr(VI)	10	0.044	2.57	1.000
Pb(II)	10	0.233	2.21	0.999

**Fig. 17: Pseudo-second order kinetic plot of Cr(VI) and Pb(II) adsorption onto B-Ppy composite**

FT-IR analysis

Fig.19 shows FT-IR spectra of bentonite, pure Ppy, and B-Ppy composite.

The spectrum of bentonite shows absorption bands located between 3200–3800 cm^{-1} , 1600-1700 cm^{-1} , and between 300-1200 cm^{-1} . The bands at 1634 cm^{-1} and 3626 cm^{-1} are attributed to vibrations of elongation of the OH group of the water of constitution plus the binding vibrations of the adsorbed water, the band located at 3440 characterizes the vibrations of deformation of the H_2O molecules. The strong band at 1041 cm^{-1} and the bands at 914.2 and 848.6 cm^{-1} correspond to ν Si-O-Si, δ Al-Al-OH, and δ Al-Mg-OH respectively, characteristic bands of bentonite [45].

For the Ppy spectrum, the absorption bands at 1554, 1468, 1294 and 1189 cm^{-1} are attributed to the Ppy chain, the band at 1554 cm^{-1} is attributed to the pyrrole cycle, namely the combination, C=C and C-C, stretching vibration. The peak at 1468 cm^{-1} is associated with the C-N stretching vibration. The peak at 1294 cm^{-1} is attributed to C-H deformation vibrations. A broad strong band at about 3434 cm^{-1} corresponds to the N-H stretching vibration of the Ppy [44, 46].

The spectrum of the B-Ppy composite shows characteristic absorption peaks associated with the polypyrrole and bentonite chains, which confirms strong interactions between the bentonite and Ppy.

SEM analysis

SEM images of bentonite, pure Ppy, and B-Ppy composite at $\times 5000$ magnification are presented in Fig. 20.

The SEM micrograph of bentonite Fig. 20(a), shows a wide distribution of the sizes of the grains of small diameter, which translates a very fine granulometry of the bentonite, one also notices, the arrangement in the form of sheets in the particles of bentonite, as well as a significant presence of macropores, while polypyrrole Fig. 20(b) reveals the presence of globular particles in the form of whitish-colored agglomerates, distributed in a non-uniform manner, as already described in the literature [47].

The SEM micrograph of the composite represented in Fig.20(c) shows a significant change in morphology, where a more ordered and denser structure is observed, and small size aggregates with a high density of granules per unit area compared to the SEM image of polypyrrole Fig.20 (b) where the aggregates are larger in size with less density per unit area. This shows that increasing the loading rate in the composite increases the compactness of the samples which become denser. It is also noted that the clay particles are not observed on the surface of the composite. This suggests that, during in situ polymerization, the clay particles were covered by the polymer chains, which may be facilitated by an attractive interaction between the bentonite surface and the Ppy. The latter is optionally bonded to the surface by a hydrogen bond between the amino groups of the Ppy chains and the oxygen

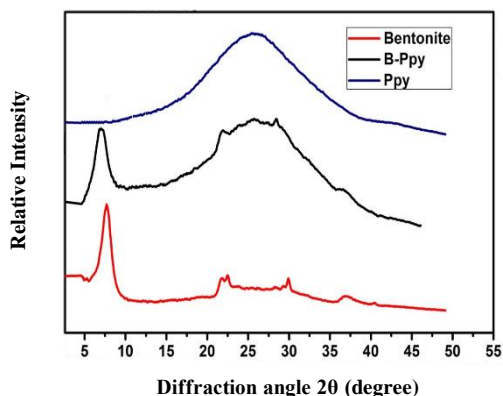


Fig. 18: XRD of bentonite, Ppy and B-Ppy composite.

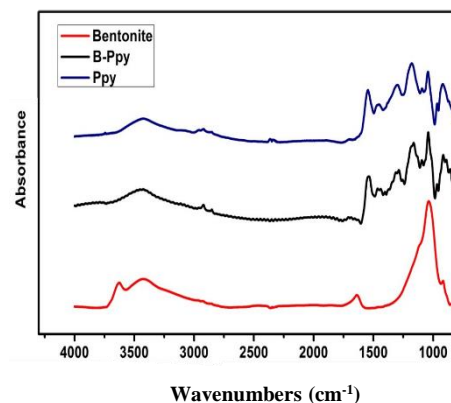


Fig. 19: FT-IR spectra of of bentonite, Ppy and B-Ppy.

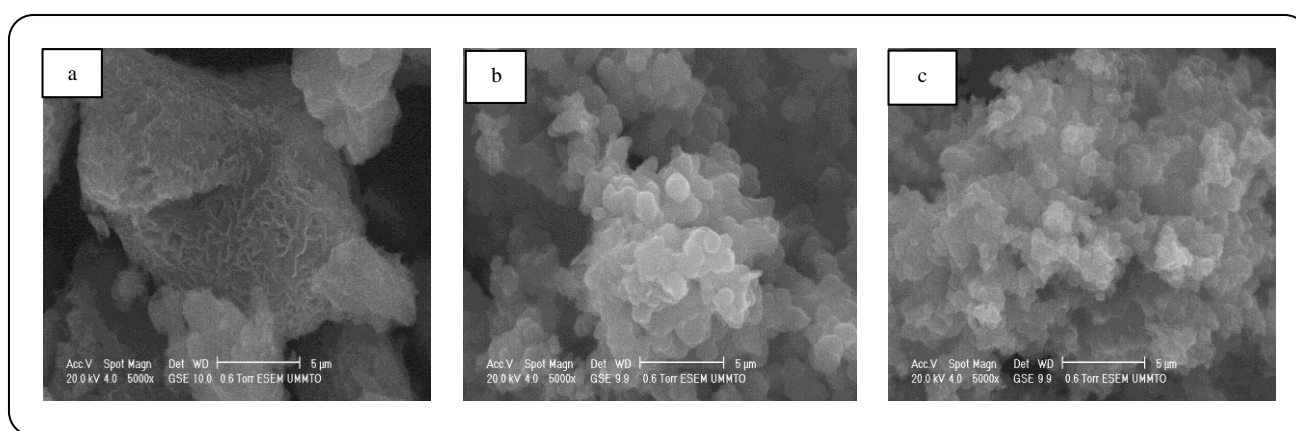


Fig. 20: SEM micrographs (magnification×5000) of (a) Bentonite, (b) Ppy, and (c) B-Ppy.

on the surface of the bentonite. This morphological pattern has also been observed by other researchers [44, 48].

Regeneration of B-Ppy composite material

For the regeneration of the B-Ppy composite, we carried out desorption tests using a solution of NaOH (2M). The method used consists of stirring a quantity of composite in the basic solution (1 g of composite in 100 mL of sodium hydroxide) for 60 min, and then assaying the concentration of metal cations in this solution after filtration. The regenerated composite is then used to perform a new adsorption test. Adsorption capacities identical to those obtained during the first test were detected. This result then led us to study the effect of the number of cycles (number of times) of adsorption-desorption of metal cations to determine the regeneration efficiency. The results in Fig. 21 show that the quantities of adsorbed and desorbed cations for the same cycle are practically equal with a slight decrease during regeneration for the 5 cycles carried out.

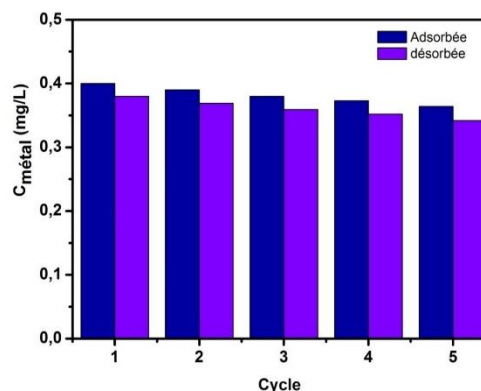


Fig. 21: Quantities of metal adsorbed and desorbed during 5 adsorption-desorption cycles.

CONCLUSIONS

Our work focuses on the adsorption of metal ions Cr^{6+} and Pb^{2+} in aqueous solution on a Bentonite-Polypyrrole composite chemically synthesized and washed with water and acetone to remove excess monomer. We performed

our tests under laboratory conditions on synthetic solutions using a batch adsorption technique. We studied the effect of pH, contact time, initial concentration, variation of the zeta potential, the effect of common ions and organic matter on the adsorption capacity of the composite. The results showed that the composite exhibits appreciable adsorbing power with respect to heavy metals.

The study of the effect of pH, contact time and that of the initial concentration of metal ions showed that the composite is more effective at a contact time of 60 min, an initial concentration of 10mg/L, and a pH of 2 for the adsorption of Cr(VI) and 5 for the adsorption of Pb(II).

Measurements of the electrokinetic potential on the composite before and after adsorption of the metal cations show that the isoelectric point or the zero charge point ZPC shifts to higher pH values during adsorption, and that the electrokinetic potential of the composite having fixed metal cations is greater than that of the corresponding composite.

The study of the adsorption as a function of the increasing contents of sodium and calcium salts added simultaneously to those of the metal ions, shows that the maximum exchange capacity with respect to these metals decreases regularly when the contents of other salts increase. In wastewater, there will be competition between the major cations present and the polluting cations for adsorption on the B-Ppy composite. The affinity of the composite is greater for sodium than for calcium and the efficiency of depollution by the composite is lower the more strongly the medium is mineralized.

The presence of Humic Acids (HA) can affect the adsorption behavior of metal cations and disrupt the adsorption conditions, changing the surface characteristics of the composite and/or forming complexes with metals dissolved in solution.

The Spectral analyses by X-ray diffraction and Fourier transform infrared, as well as microscopic observations at the SEM confirm the intercalation of Ppy in the inner layers of the bentonite.

Langmuir and Freundlich's isotherms were used to describe the adsorption of metal cations, the results obtained showed that both models were applicable, with a preponderance of Langmuir-type isotherms. The correlation coefficients for linear studies exceed 98% for both models. They also show that the affinity of the composite towards the two heavy metals is in the order: Cr > Pb.

The kinetics of adsorption were determined using the pseudo-second-order model. The correlation coefficients (higher than 0.999) indicate good compliance of the experimental data with the proposed pseudo-second-order kinetic model.

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