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Adsorption of Cadmium onto modified bentonites from aqueous solutions

M. Djab, B. Makhoukhi*

Laboratory of separation and purification technologies, Tlemcen university, B.P 119, Algeria.

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benamarmakh@yahoo.fr
Phone: +213774008003

Abstract

The exchange of clay ions using salts of bis-imidazolium (MBM) could submit clay organophilic materials which permit an effective conservation of cadmium in aqueous solution.Imidazolium salts have already been used successfully for this purpose. Due this hydrophobicity, organo clays will be expected to behave as effective sorbent for organic pollutants, more particularly those having low solubility**.** For this purpose, the present study treats with bentonite modification MBM–Bt using para, meta and ortho bis-imidazolium salts and tries to retain harmful very toxic inorganic metal. The experiments on cadmium with different bentonites show increase of the maximum uptake capacities (q_m) from 3.65, 4.48, and 7.12 $mg.g^{-1}$ for o-MBM–Bt, m-MBM–Bt, p-MBM–Bt respectively. To provide the best description of cadmium adsorption behaviour we use different type of adsorption isotherms and kinetic models. According to the results obtained Langmuir model and the pseudo-second order are the most appropriate. The findings reported in this study aid in facilitating the extraction of cadmium resources from aqueous using modified bentonites.

1. Introduction

Environmental pollution is one of greatest challenges that world is facing today. It began since industrial revolution, increasing day by day and causing irreparable damage to Mother Earth. Environmental pollution has its own causes, effects and solutions. For this we must eliminate the heavy metals from industrial effluents before discharging waste aqueous solution into environment [1-7].

The cadmium has been considered one of the most toxic heavy metals due of their non-biodegradability, bioaccumulation in the water and carcinogenic nature [8-10]. A cadmium metal is note very reactive; it reacts slowly to moist air and, with heating, oxygen, sulfur, phosphorus and halogens. It is attacked by non-oxidizing acids. Cadmium pollution comes mainly from the electroplating industry, production of alkaline batteries, plastics and pigments industries. As consequence, that pollution is present everywhere in the environment; prolonged exposure causes severe damage to human health [11]. Therefore and there have been many researchers in this field to remediate the soil and water from cadmium pollution. For this, many adsorbents have been used like syzygiumcumini leaf powder [12], iron or slime [13], pen shells [14] and dithiocarbamate functionalized pyrrole based terpolymers [15] to reduce pollution. Several chemical and physical technologies are used and developed to treat heavy metals in wastewater, among the present technologies; Adsorption is a wastewater purification technique for removing a wide range of compounds from industrial wastewater. Adsorption is most commonly implemented for the removal or low concentrations of non-degradable organic compounds from groundwater, drinking water preparation, process water or as tertiary cleansing after, for example, biological water purification [16].

Bentonite is clay which is an absorbent aluminum phyllosilicate consisting mostly of montmorillonite content which represents a 2:1 dioctahedral smectite. It is a chemically inert, non-corrosive. It is the most economical and efficient desiccant bag-filling material. Some Algerian bentonites have been proposed to be used in drilling of oil wells [17], herbicides [18], in sorption of metals [19], catalysis [20], and sorption of dyes [21]. The isomorphic substitutions of Al^{3+} for Si^{4+} in the tetrahedral layer, and Mg^{2+} for Al^{3+} in the octahedral layer constitutes permanent negatives layer charge. This type of layer charge is expressed at the basal or interlayer surface and is neutralized by the exchange cations (Ca^{2+}, Na^{+}, etc.). The chemical treatment of clay

minerals offers us adsorbents of organic compounds [22,23]. The modified clays are very efficient in adsorbing ionic or polar compounds, but week in non-ionic and non-polar compounds like heavy metals [24]. This last are more favorably adsorbed by organic matter than by clay [25].

The present investigation treats modification of the bentonites with different organic salts followed by a structural characterization for all the samples. Thus, our study is deal the possibility of modification in the adsorption capacity of cadmium, in addition the role of the surface treatments. The factors affecting adsorption are investigated (pH, contact time, etc.) the adsorption capacity of cadmium is studies using the pseudo-first order and pseudo-second order.

2. Material and Methods

2.1. Bentonite simple

The chemical composition of bentonite determined by X-ray fluorescence spectroscopy (Phiplis PW 3710) and was found to be as follows: 62.48% SiO_2, 17.53% Al_2O_3, 1.23% Fe_2O_3, 3.59% MgO, 0.82% K_2O, 0.87% CaO, 0.22% TiO_2, 0.39% Na_2O, 0.04% As and 13.0% loss [4]. According to the results by X-ray fluorescence spectroscopy montmorillonite represents the highest percentage in the composition of our clay (86%wt); followed by quartz (10%), cristobalite (3.0%) and beidellite (≥1%) [26-28].

For purification of bentonite, the stirring for 15 min 120 g of natural bentonite in 1.5 L of distilled water was followed by adding a sodium citrate buffer solution (pH = 7). The mixture was heated under agitation at 75°C during 20 min and then, 15 g of sodium thiosulfate ($Na_2S_2O_4$) was slowly added over 15 min. the solid recovered after centrifugation at a speed of 6000 rpm (JA centrifugal type 10) was washed twice with 0.05 M HCl (1.5 L) for 3 h.

To set the sodium form of the pure bentonite, the mas ratio of the bentonite to NaCl solution (1M) is 1/5, and after agitation for 2h, Na-Bt was centrifuged at a rotational speed of 6000 rpm for 20 min; followed by washing with distilled water 3 times and finishing by drying. Chemical composition of purified bentonite gave us the following results: 64.7% SiO_2, 18.1% Al_2O_3, 0.95% Fe_2O_3, 2.66% MgO, 0.8% K_2O, 0.61% CaO, 0.2% TiO_2, 1.43% Na_2O, 0.05% As and 10.0% loss. The cation exchange capacity (CEC) was 0.98 meq per 100 g of dry Na-Bt. The specific surface area increases from 50 m^2/g in Bt to 95 m^2/g in Na-Bt [4,5].

The X-ray diffraction pattern of Bt-Na^+ was compared to that of the natural bentonite, as illustrated by (Fig. 1). It clearly appears that the clay mineral crystallinity of Bt-Na^+ was not diminished upon purification. The Figure 1 shows the XRD pattern of natural bentonite and Bt-Na^+ was exhibiting the reflection peak occurred at 6.1° and 6.7°, respectively. The interlayer spacing distance of the bentonites was found to be 14.5 Å and 13.2 Å, respectively. The decrease in the interlayer spacing of Bt-Na^+ was due to cationic exchange of Ca^{2+}, Mg^{2+} and K^+ cations, replaced by Na^+ cations which have a smaller atomic radius.

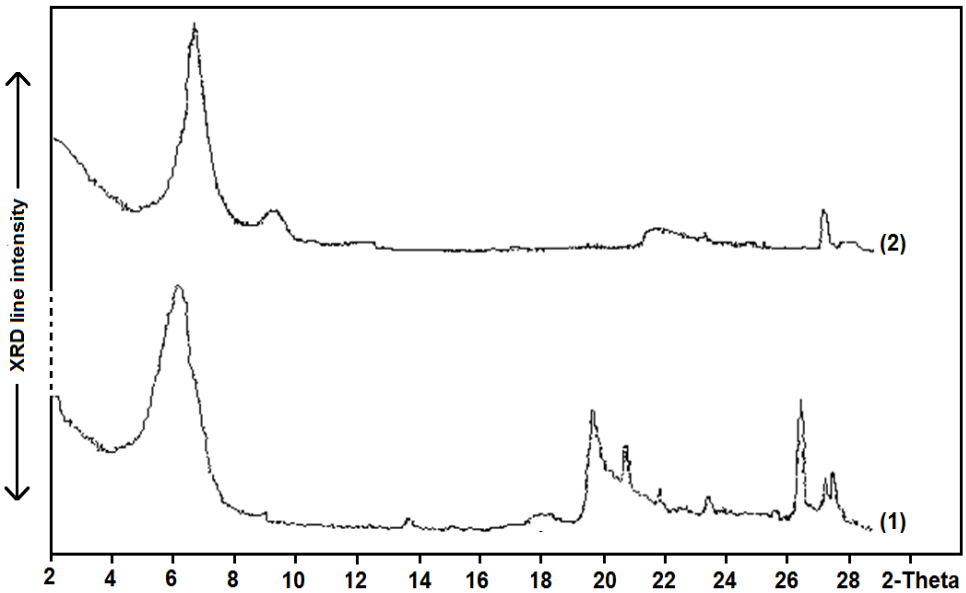

Figure 1: XRD patterns for bentonites before and after purification: (1) Natural bentonite; (2) Bt-Na^+.

The X-ray diffraction pattern of bentonites confirms that bentonite was purified. We observed the disappearance of some characteristic reflection peak of crystalline phases of impurities especially that of quartz located at 2θ= 26.8°. Also, we observed the intensification of some reflection peak localized at 2θ= 5.7 and 28°.

2.2. Synthesis of bis-imidazolium salts

A mixture of bis(chloromethyl) benzene (1.748 g; 10 mmol.) and 1-methyl imidazole (1.64 g; 20 mmol.) in DMF (40 mL) were heated and stirred at 120°C for 8 h. A precipitate of salt was formed while the mixture was hot. After cooling (20°C), the solution was filtered under vacuum, and the solid was washed with dry diethyl ether (100 mL). The product precipitate was dried under vacuum at 20°C for 1 h [6].

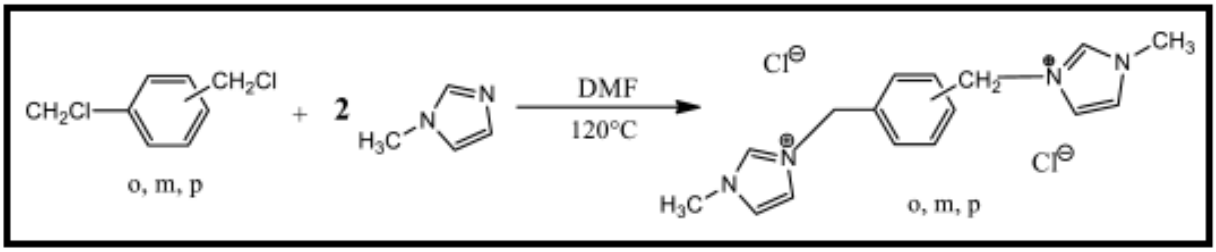

Figure 2: Synthesis of bisimidazolium dichloride (MBM) (o: ortho m: metha p: para).

Three salts were synthesized and characterized: para, mata and ortho ((1,4 phenylenebis(methylene))bis(1-methyl-1*H*-imidazol-3-ium) dichloride).

Table 1: Characterization of bisimidazolium salts.

	p-MBM	**m-MBM**	**o-MBM**
Yield (%)	91 %	81 %	92 %
^{1}H NMR (D_2O) δ_H (ppm)	3.67 (CH_3, 6H, d), 5.25 (CH_2, 4H, d), 7.28 (4H, m), 7.49 (2H, t), 7.56 (2H, t), 9.06 (2H, s)	3.87(CH_3, 6H, d), 5.41(CH_2, 4H, d), 7.50 (4H, m), 7.69(2H, t), 8.57(2H, s), 9.16(2H, s)	3.82(CH_3, 6H, d), 5.42 (CH_2, 4H, d), 7.41 (4H, m), 7.47(2H, t), 7.56 (2H, m), 8.95(2H, s)
^{13}C NMR (D_2O) δ_C (ppm)	2C (35.68), $4C_{imd}$ (52.24), $2C_{arm}$ (120.90), $4C_{arm}$ (130.08), $2C_{imd}$ (135.38)	2C (35.66), 2C (52.34), $4C_{imd}$ (122.12), $4C_{arm}$ (127.67), $2C_{imd}$ (129.15), $2C_{arm}$ (133.18)	2C (35.66), 2C (52.36), $4C_{imd}$ (123.77), $2C_{arm}$ (127.50), $2C_{arm}$ (129.15), $2C_{imd}$(133.18), $2C_{arm}$(140.43)
FTIR ν (cm^{-1})	730-857 (C–H), 1163(C–N), 1335(CH_3), 1542(C=arm), 1560 (C=N)	753-805 (C–H), 1160(C–N), 1355 (CH_3), 1542(C=arm), 1633 (C=N)	763-885 (C–H), 1170 (C–N), 1360 (CH_3), 1442(C=arm), 1643 (C=N)

2.3. Preparation of organo-clays

The bentonite was modified to improve the anions adsorption capacity by reacting the cation surfactant of bisimidazolium cations into Na-Bt following a previously described procedure: stirring 100 ml of hot distilled water we mixed 5 g of Na-Bt with 0.85 g of bisimidazolium salt (2.5 mmol). The preparation was consistently agitated for 24h at 60°C. After agitation, the solid centrifuged and washed by distilled water 3 times with distilled water and finalized by drying at 80°C.

2.4. Analytical methods

The adsorption of cadmium ions was studied by the batch method under different operating conditions. The synthetic metal solutions were prepared using metal salts $CdCl_2$ dissolved in distilled water. In an adsorption experiment, in a test tube we mixed quantity of 0.2 g Na-Bt with 20 ml of a known concentration of cadmium solution with stirring. We used NaOH or 0.1 M HCl to adjust the pH with a pH meter HANNA instrument. After a contact time, sufficient to reach equilibrium, the collected metallic solution was recovered by centrifugation and then analyzed by Analytik Jena (SPECORD210) UV-vis spectrophotometer.

Adsorption kinetics was studied at 20 ± 1°C. Amounts of 0.2 g of Na-Bt and organo-Bt mixed with 10 mL of 100 $mg.L^{-1}$ cadmium solutions under agitation ranging from 0 to 300 min. To study the influence of pH, we have taken an interval of 2 to 8. The effect of initial metal concentration was studied using initial concentrations changing from 0.5 to 5 $mg.L^{-1}$. Iodine potassium was chosen as the salt model for studying the influence on the sorption ranging from 0.005 to 0.1 M and finally the adsorption process was studied at different temperatures 20, 35 and 50°C.

2.5. Characterizations methods

The X-ray fluorescence spectroscopy (Philips PW 3710) gave us the chemical composition of our simple, IR spectra were obtained with solids or neat liquids with a PerkinElmer 16 PC spectrometer model Fourier transform infrared pectrometer with ATR accessory.

The NMR spectra were recorded in D_2O, with Fourier Bruker AC 400 multinuclear spectrometer. XRD results was taken by Philips X-Pert diffractometer using Ni filtered Cu-Ka radiation and for the thermogravimetric analyses (TGA) we have used a PerkinElmer TGA7 thermogravimetric analyze.

3. Results & discussion

3.1. Characteristic results for organo-Bt

3.1.1. XRD analysis

XRD pattern of raw bentonite (Figure 3a), showed the d_{001} reflection of Na-Bt, p-MBM–Bt, m-MBM–Bt and o-MBM–Bt at 2theta = 4.8°, 6.9°, 5.5°and, 5.2° respectively. After the intercalation, the results gave us 12.9 Å, 19.53 Å, 17.88 Å and 16.05 Å, respectively. This indicated that organic cations have been well intercalated in interspace. The results show a difference between the modified bentonites, the increase in space in p-MBM–Bt is greater than m-MBM–Bt which is more than o-MBM–Bt. The difference for these bentonites is due to the difference in the size of organic salts and their organization in the interlayer spacing [29].

3.1.2. TG analysis

Concerning the dried bentonite curve (Figure 3b), 9.5% weight-loss was checked at the temperature range of 20–200°C and 4.75% weight-loss appeared at 200–800°C. The first is due to the evaporation of the desorbed water, which was adsorbed onto the cations in the bentonite interlayer. The second is related to the removal of water molecules from the crystal lattice, with one alumina octahedral sheet sandwiched between two silica tetrahedral sheets.

Concerning the modified bentonites, the weight loss due to the presence of product in the bentonites is clearly noticed. Figure (3b) combines the TGA curves for bentonite and p-MBM–Bt investigated and shows the corresponding derivative weight loss curves. At the temperature range of 350–400°C, a thermal decomposition of bis-imidazolium cation was observed with a weight loss of up to 90%. In the temperature zone 300-500°C, the DTG curves showed us exothermic peaks. The beginning of the first isotherm due when the bis-imidazolium salts begins to decompose [29]. For the TGA of o-MBM–Bt and m-MBM–Bt, we observed the same behavior as that of p-MBM–Bt.

3.1.3. FTIR analysis

FTIR is a qualitative technique, the best way to understand the peaks depends on the functional groups, clays display a number of adsorption peaks, reflecting the complex nature of clays (Figure 3c). The main band observed are —OH stretching derived from M—OH (M=Al, Fe, Mg and Si) they are shown at 3620–3640 cm^{-1}. These bands associated to stretching vibrations O—H groups coordinated to two Al atoms (3620 cm^{-1}) or Al and Mg atoms (3640 cm^{-1}) in octahedral sheets of bentonite. For the band centered at 1027 cm^{-1} assigned to the Si—O vibration within the layer which is related to the M—O stretching vibration (M=Al, Mg and Fe) located in octahedral sheets appear at 400–550 cm^{-1} range. The FTIR spectrum shows a band in the region 3000-3100 cm^{-1} which is characteristic of the vibration of aromatic C—H of imidazolium salts. Other bands at 730, 830, 845, 1100, 1320, 1480, 1510 and 1580 cm^{-1} confirm the presence of bisimidazolium in the molecular structure [29].

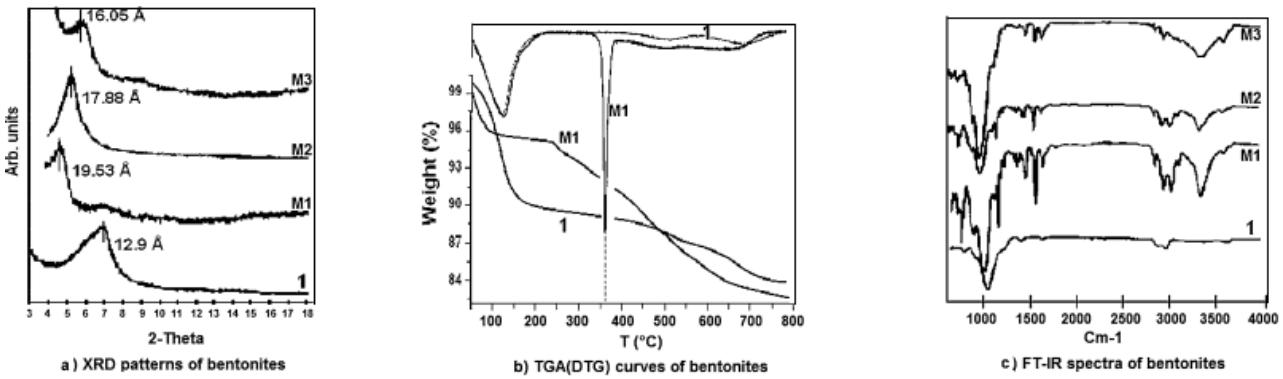

Figure 3: Characterization of Na-Bt and organo-Bt. (1) Na-Bt; (M1) p-MBM-Bt; (M2) m-MBM-Bt; (M3) o-MBM-Bt

3.2. The effect of pH

The study the effect of pH is considered one of the most important factors among other factors [30]. The results of the influence of pH on the adsorption of cadmium by the various bentonites were presented in (Figure 4). The maximum adsorption of 81.32%, 76.04%, 86.14%, 53.98% for p-MBM–Bt,m-MBM–Bt,o-MBM–Bt and Na-Bt took place at pH = 5. From the results obtained it is observed that there is a reciprocal relationship between pH and cadmium adsorption due to the higher protonation of modified bentonite compared to sodium bentonite. This protonation, on the surface of bentonite modified between the ions gives an electrostatic attraction which had affected the surface complexation reaction [31,32].

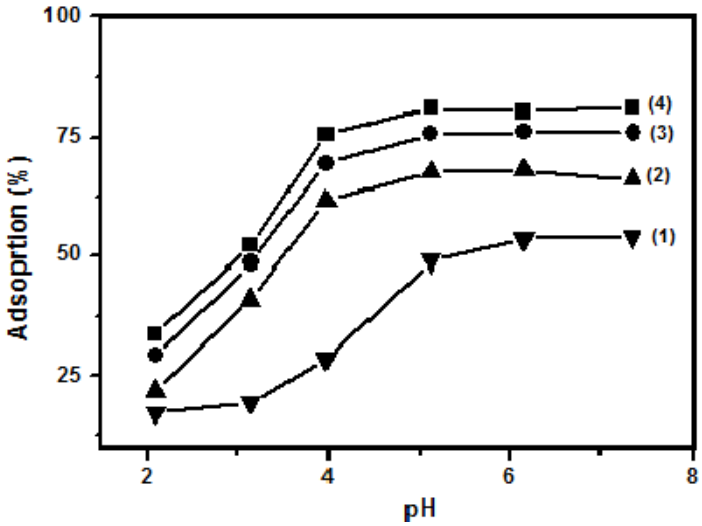

Figure 4: Removal of Cd(II) as a function of pH. (1) p-MBM-Bt; (2) m-MBM-Bt; (3) o-MBM-Bt; (4) Na-Bt.

3.3. Effect of initial concentration

According to the above effect, pH = 5 was worn to study the initial concentration effect on cadmium adsorption by the different bentonites under a stirring speed of 800 rpm for 3 hours. As shown in (Figure 5), the adsorption efficiency increased significantly with increasing the concentration of adsorbent up to 1 $g.L^{-1}$. And subsequent concentrations, the adsorption efficiency decreases. This is due to the following reasons:

Increased number of adsorption site per unit mass depending on adsorbent concentration allows comparatively high adsorption and at great adsorbent concentration creates particle aggregation and decrease in specific surface area, as a result, increase in diffusional path leads to low adsorption efficiency [33].

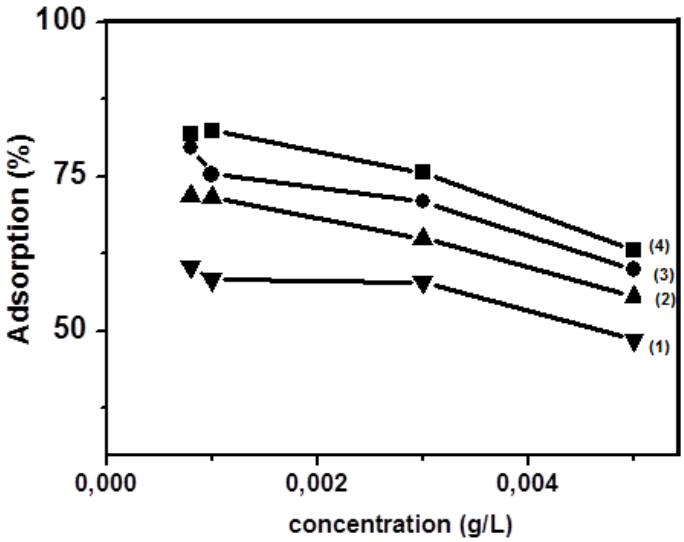

Figure 5: Removal of Cd(II) as a function of initial concentration.
(1) p-MBM-Bt; (2) m-MBM-Bt; (3) o-MBM-Bt; (4) Na-Bt.

3.4. Effect of contact times

To study the contact time of adsorption of heavy metal by the various bentonites, pH = 5 was selected with an initial cadmium concentration of 20 $mg.L^{-1}$ at room temperature. The results proofs that the initial

adsorption of Cd (II) was rapid onto the modified bentonites. The equilibrium was reached at 30 min, 60 min and 60 min for p-MBM–Bt,m-MBM–Bt and o-MBM–Bt respectively. The selected metal ions are recovered by the adsorption sites on the different bentonite; adsorption efficiency was connected on the transportation average of Cd (II) from the solution to adsorption sites [33]. The increase in salts concentration reduces the electrostatic repulsion between the Cd (II) ions and the surface of bentonites, which gives us an increase in the collisions between the Cd (II) ions and bentonites [34].

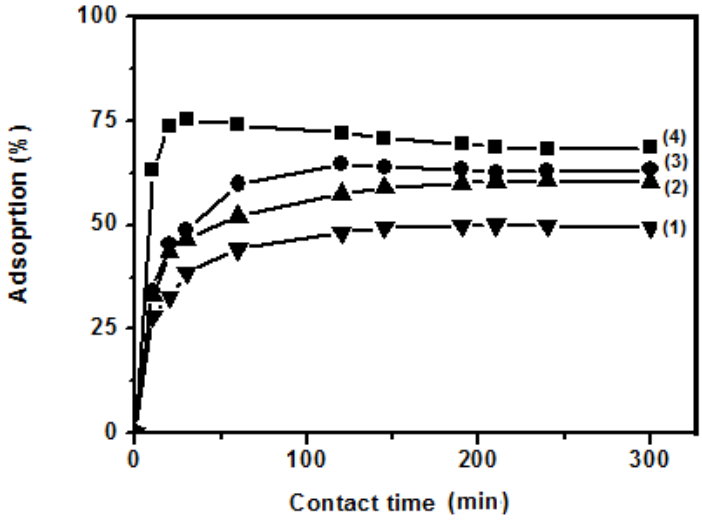

Figure 6: Removal of Cd(II) as a function time. (1) p-MBM-Bt; (2) m-MBM-Bt; (3) o-MBM-Bt; (4) Na-Bt.

3.5. Effect of the salt concentration

It is known that salts have significant effect on the adsorption process. In this work of potassium iodide (KI) was chosen as the salt model for studying the influence on the sorption of cadmium by modified bentonites. That is why a series of solutions was exposed containing salt in the concentration range of 0.005 to 0.1 M.

The cadmium removal efficiency increased from 1.37% to 35.67%, 48% to 75.83%, 50.54% to 80.68% and 53.13% to 89.88% for Na-Bt, o-MBM–Bt, m-MBM–Bt and p-MBM–Bt (Figure 7). Addition of KI increased the adsorption yield of cadmium, which is explained by the increase in the sites of the different bentonites which has been active by the increase in salt concentration.

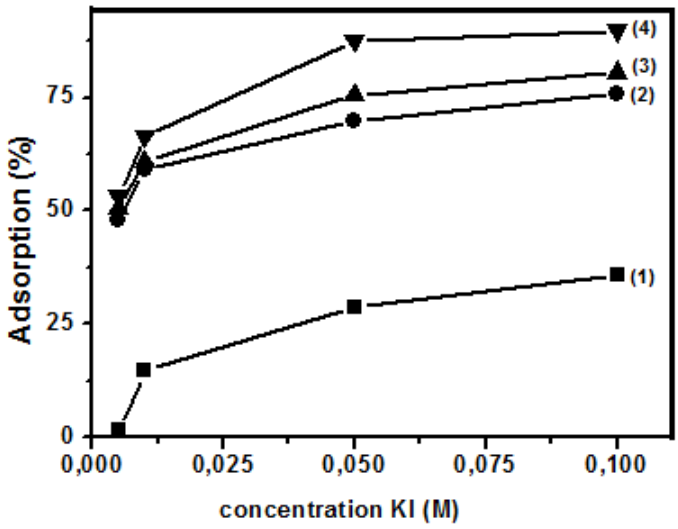

Figure 7: Removal of Cd(II) as a function salt concentration. (1) p-MBM-Bt; (2) m-MBM-Bt; (3) o-MBM-Bt; (4) Na-Bt

3.6. Adsorption isotherms

Adsorption process is usually studies through graphs known as adsorption isotherm. It is the relationship between the pressure and amount at a constant temperature. There have been a large number of mechanisms and models devised and proposed to explain adsorption phenomena. The salient ones are selected in this study [35]:

3.6.1. Langmuir model

The Langmuir model is based on five principal assumptions:

The gas phase and adsorbed phase are in equilibrium, no interactions are present between molecules once adsorbed, adsorption is independent of local surface coverage, solid surface is homogeneous with all adsorption sites equivalent and no phase transition is taking place.

In this model, the rate of adsorption is taken to be proportional to the component partial pressure, and leads to the result:

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad (1)$$

Where C_e is the equilibrium concentration of cadmium (mgL^{-1}), $q_e$is the adsorption capacity ($mg.g^{-1}$), q_m the maximum adsorption of cadmium ($mg.g^{-1}$), K_L is the Langmuir adsorption constant ($mg.g^{-1}$). The values of q_m and K_L are calculated from the slope and intercept of linear plot of C_e/q_e against C_e.

3.6.2. Freundlich isotherm

Freundlich adsorption isotherm is obeyed by the adsorption where the adsorbate forms a monomolecular layer on the surface of the adsorbent.

$$\log q_e = \log K_F + 1/n \ \log C_e \qquad (2)$$

Where K_F is the Freundlich adsorption constants and (1/n) is the intensity of adsorption.

The results are shown in Table 2. On basis on these data values obtained from adsorption adopted the both model. However, Langmuir described better than Freundlich isotherm in comparison with correlation coefficient of each one.

The maximum adsorption capacity (q_m) of p-MBM–Bt, m-MBM–Bt and o-MBM–Bt for Cd (II) was estimated to be 3.65, 4.48 and 7.12 $mg.g^{-1}$, respectively. This difference is due to an increase in the charter organophilic for the cadmium. The p-MBM–Bt was the materiel with higher adsorption capacity compared with the other adsorbents. This increase in q_m, can be explained by an increase in interlayer space which gives a better diffusion [36]. Table 2 shows a comparison of q_m for cadmium onto various bentonites. The adsorption capacity of p-MBM–Bt, m-MBM–Bt and o-MBM–Bt is comparable with those of other adsorbents.

Table 2: Parameters of Langmuir and Freundlich models for the adsorption of Cd (II).

Adsorbate	Absorbent	Langmuir isotherm			Freundlich isotherm		
		K_L	q_m^{-1}	R^2	q_m^{-1}	1/n	R^2
Cd(II)	Na–Bt	2.46	1.565	0.955	9.64	1.01	0.864
	p-MBM–Bt	7.12	3.674	0.984	4.33	1.03	0.768
	m-MBM–Bt	4.48	5.220	0.976	7.15	1.09	0.850
	o-MBM–Bt	3.65	2.296	0.969	9.34	1.09	0.864

3.7. Adsorption kinetics models

In order to determine the mechanism of heavy metal onto bentonites. In this study, two kinetic model equations are exercised to quest the kinetic of Cd(II) adsorption onto modified bentonites.

Pseudo-first-order model rate expression known as the Lagergren assumes that the physical adsorption is the origin of the bonds, the linear in expressed as:

$$\text{Log}\ (q_e - q_t) = \log q_e - k_f (t/2.303) \qquad (3)$$

Where q_t ($mg.g^{-1}$) is the amount of Cd (II) adsorbed at time t, q_e (mg/g) is the amount of Cd(II) adsorbed at equilibrium. The k_f (min^{-1}) is the constant of pseudo-first order kinetics that is calculated from the slope on the linear plot shown in (Figure 8).

Pseudo-second order model assumes that the chemical adsorption is the origin of the bonds the linear in expressed as:

$$t/q_t = 1/k_s q_e^2 + (t/q_e) \qquad (4)$$

Where q_t ($mg.g^{-1}$) is the amount of Cd (II) adsorbed at time t, q_e ($mg.g^{-1}$) is the amount of Cd(II) adsorbed at equilibrium. The k_s (min^{-1}) is the constant of pseudo-second order kinetics, who is calculated from the slope on the linear plot shown in (figure 8).

The kinetic parameters were listed in Table 3. It was observed that the correlation coefficient of the pseudo-second-order model ($R^2 \geq 0.99$) were better than those of pseudo-first order, this confirms that the adsorption of cadmium onto different bentonites depend on chemical adsorption. In the case when the participating species interact chemically, adsorption takes place by means of formation of chemical bonds.

Table 3: Kinetics model of adsorption of Cd(II).

Bentonite	1st order (PFO)			2nd order (PSO)		
	q_{1e} (mgg^{-1})	k_f (min^{-1})	R^2	q_{2e} (mgg^{-1})	k_s ($gmg^{-1}min^{-1}$)	R^2
Na–Bt	0.628	0.036	0.98	18.85	0.074	0.99
p-MBM–Bt	1.024	0.024	0.99	25.13	0.17	0.99
m-MBM–Bt	0.891	0.189	0.96	22.86	0.057	0.99
o-MBM–Bt	0.907	0.022	0.96	23.78	0.086	0.99

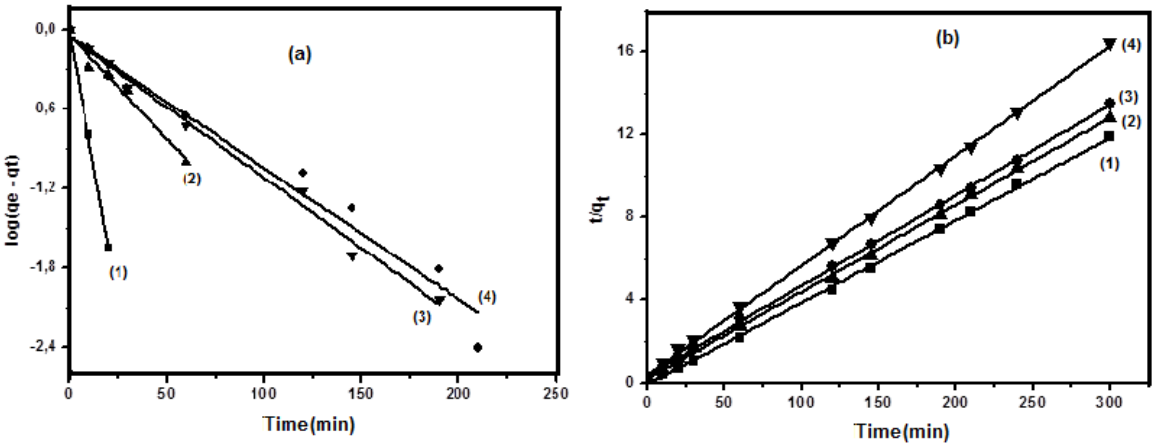

Figure 8: Modeling of adsorption kinetics, (a) pseudo-first order; (b) pseudo-second order
(1) p-MBM-Bt; (2) m-MBM-Bt; (3) o-MBM-Bt; (4) Na-Bt.

3.8. Comparative study

Based on previous relevant researches, a comparison of the adsorption capacities Cd(II) was studied in this field[37-42]. As obviously, especially the prepared bentonites have a comparable adsorption capacity and thus ca be deemed as potent adsorbent for the adsorption of selected ions metallic from aqueous solutions. Increase in the adsorption capacity of cadmium ions by the modified bentonite samples can be explained by several factors, modified adsorbent surface, the method of removing heavy metals (pH, initial concentration, contact time). Nevertheless, the bentonites prepared in this work promise an effective and cheap adsorbent for the removal of cadmium ions from aqueous solution.

Conclusion

In this study, bentonites intercalation with bis-imidazolium salts was confirmed by FTIR spectroscopy and X-Ray Diffraction. The experiments showed an increase in the affinity for the adsorption of the selected heavy metal. The p-MBM–Bt displayed higher effectiveness than m-MBM–Bt and o-MBM–Bt in cadmium retention.

The various parameters applied to the adsorption of cadmium in the aqueous solutions show a remarkable improvement in the capacity of the adsorption of heavy metal by our modified bentonites. The adsorption of cadmium ion depends on pseudo-second order kinetic model, while the Langmuir model is the appropriate model for adsorption isotherm; the latter exhibits a sorption capacity of 7.12 $mg.g^{-1}$, 4.48 $mg.g^{-1}$ and 3.65 $mg.g^{-1}$ for p-MBM–Bt, m-MBM–Bt and o-MBM–Bt, respectively. Moreover, based on all results the prepared bentonites exhibited an effective and cheap adsorbent for removing cadmium ion from aqueous solutions because of its relatively high specifics surfaces area, adsorption capacity, repeatability performance and the advantages of ease and preparations in low-cost.

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