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Modification de la bentonite par les sels de bisimidazolium et applications à l'adsorption de colorants textiles

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Résumé

La modification d'une bentonite par intercalation des cations de bismidazolium (MBIM) pourrait fournir des matériaux argileux organophiles qui permettent une rétention efficace des colorants textiles. Le présent travail porte sur la modification de la bentonite (Bt) par les cations (ortho, méta et para) bisimidazolium et sur les tentatives d'élimination de colorants textiles synthétiques, tels que (Rouge-Telon, Orange-Telon et bleu-Telon) par adsorption, à partir de solutions aqueuses.
Les bentonites modifiées ont été caractérisées par spectroscopie infrarouge (FTIR), diffraction des rayons X (XRD) et analyse thermogravimétrique (TGA). Les tests d'adsorption appliqués aux colorants ont révélé une augmentation importante des capacités d'adsorption (de 21-28 à 88-108 mg.g-1) après intercalation. Les meilleurs rendements ont été obtenus on utilisant la bentonite modifiée par le p-MBIM pour adsorber le colorant Orange. L'équation de vitesse de pseudo-premier ordre a été en mesure de fournir la meilleure description des données de cinétique d'adsorption pour les trois colorants. Les modèles d'adsorption de Langmuir et Freundlich ont été appliqués pour décrire les isothermes d'équilibre et les constantes d'isothermes ont également été déterminées.

Mots clés: Bentonite, Bisimidazolium, Colorants textiles, Adsorption, Isotherme.

Organophilic bentonite for Telon derivatives removal from aqueous media

Abstract

Clay ion-exchange using bismidazolium salts (MBIM) could provide organophilic clays materials that allow effective retention of polluting dyes. The present investigations deal with bentonite (Bt) modification using (ortho, meta and para) bisimidazolium cations and attempts to remove a synthetic textile dyes, such as (Telon-Orange, Telon-Red and Telon-Blue) by adsorption, from aqueous solutions. The surface modification of MBIM–Bt was examined using infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). Adsorption tests applied to Telon dyes revealed a significant increase of the maximum adsorption capacity from ca. 21-28 to 88-108 mg.g-1 after intercalation. The highest adsorption level was noticed for Telon-Orange dye on the p-MBIM–Bt, presumably due higher interlayer space and better diffusion. The pseudo-first order rate equation was able to provide the best description of adsorption kinetics data for all three dyestuffs. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were also determined. The results show that MBIM–Bt could be employed as low-cost material for the removal of Telon dyes from effluents.

Keywords: Bentonite, Organoclay, Bisimidazolium, Dyes, Isotherms, Adsorption.

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INTRODUCTION

The removal of color dyes from wastewater before they are contacted with unpolluted natural water bodies is currently one of the major problems faced by the textile dyeing industry [1]. Various physical, chemical and biological processes have been used for the removal of dye from aqueous solutions; such as adsorption, chemical precipitation, ion exchange, membrane processes, biological degradation, chemical oxidation and solvent extraction [2].

In this regard, montmorillonite-rich materials like bentonites exhibit highly interesting properties, e.g. high specific surface area, cation-exchange capacity (CEC), porosity, and tendency to retain water or other polar and non-polar compounds [3]. The modification of clay surface is called as organoclay to cause to transform organophobic to strongly organophilic and therefore the adsorption capacity increases to compare with natural clay mineral and it can be used as an adsorbent for the adsorption of dyes. This kind of surfactant modified organobentonite has been used extensively for a wide variety of environmental applications [4].

The aim of the present work is to investigate the possibility of new organo-bentonites as an adsorbent for removal of Telon dyes, which is, namely Red, Blue and Orange, from aqueous solution by adsorption method. Thus, organo-bentonites containing different organic cations (para, meta or ortho) bisimidazolium dichloride (MBIM) were prepared. The organobentonites were characterized by FTIR spectroscopic technique, powder X-ray diffraction analysis and thermogravimetric analysis. The adsorption capacity of Telon dyes with modified bentonites was carried out using two kinetic models, which are the pseudo-second-order and first order. Finally, the experimental data were compared sing two isotherm equation, which are Langmuir and Freundlich.

2. MATERIALS AND METHODS

2.1. *Bentonite sample*

The natural bentonite used in this study was obtained from deposits in the area of Maghnia, Algeria. The chemical composition determined by X-ray fluorescence spectroscopy (PHILIPS PW 3710) was found to be as follows: 62.4% SiO_2, 17.33% Al_2O_3, 1.2% Fe_2O_3, 3.56% MgO, 0.8% K_2O, 0.81% CaO, 0.2% TiO_2, 0.33% Na_2O, 0.05% As, 13.0% loss on ignition at 900°C. The mineralogical analysis showed that the native crude clay mineral contains preponderantly montmorillonite (Mt), in a proportion exceeding 85 wt.%. The clay composition also includes quartz (10 wt.%), cristoballite (4.0 wt.%) and beidellite (less than 1 wt.%) [5].

2.2. *Synthesis of Bis-imidazolium salts*

Synthesis of bisimidazolium salts were based on the reaction of bis(chloromethyl) benzenes (1 eq) with imidazoles (2 eq) in dimethylformamide (DMF) as solvent [6].

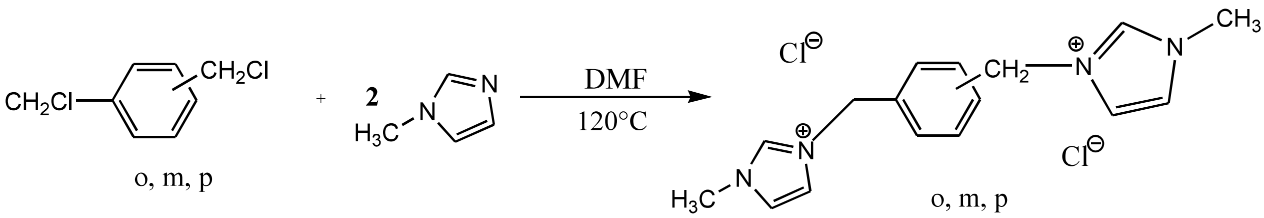

Fig. 1 - Synthesis of bis-imidazolium dichloride

2.3. *Preparation of Organo-clays*

The intercalation of the bis-imidazolium salts into the Na-Bt galleries was carried out by cationic exchange reaction following a previously described procedure: 10 g of Na-Bt were dispersed into 200 ml of hot water under continuous stirring. Then 50 mmole of bis-imidazolium salt was added under strong stirring [7].

The XRD pattern of crude Na-Bt, p.MBIM-Bt, m.MBIM-Bt and o.MBIM-Bt were exhibiting the reflection peak occurred at 6.9°, 4.8°, 5.2° and 5.5°, respectively. The interlayer spacing distance of the clays was found to be

12.8, 19.53, 18.4 and 16.05 Å, respectively. The interlayer spacing of bisimidazolium-Bt clays was found to be higher than the crude bentonite clay. The IR spectra of the intercalated bentonites reveal the presence of characteristic absorption bands of both inorganic and organic components, the characteristic bands of the initial bentonite remaining unaffected (*i.e.* band at 991 cm^{-1} can be associated at Si–O stretching vibrations) [8].

The onset temperatures of degradation for the different organoclays are derived from DTGA curves at the point where the derivative weight loss increases. The DTGA curves in region between (300-500 °C) are characterised by an exothermic peaks. The temperature at the onset of the first (prominent) isotherm is taken to represent the point at which the intercalated surfactant begins to decompose [9]. For the partially exchanged MBIM-bentonite this peak has a maximum (T_{max}) at 360°C.

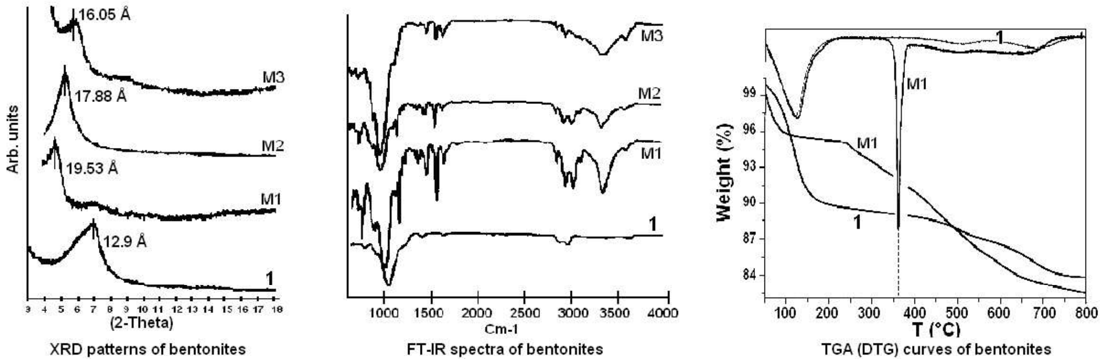

Fig. 2 - Characterization of bentonites before and after modification.
(1)Bt; (M1) p.MBIM–Bt; (M2) m.MBIM–Bt; (M3) o.MBIM–Bt

3. RESULTS AND DISCUSSIONS

3.1. *Dye adsorption over Na-Bt*

In an attempt to express the mechanism of dyes adsorption onto the Na-Bt, the following kinetic model equations are used to analyze the adsorption experimental data for determination of the related kinetic parameters.

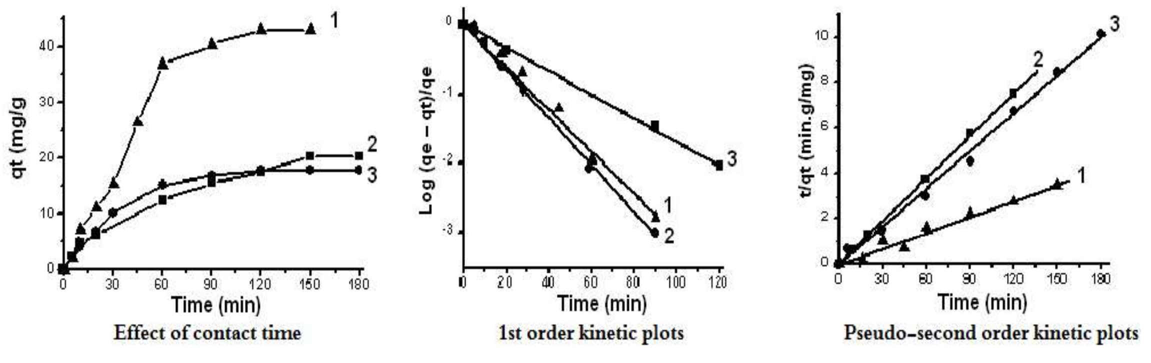

Fig. 3 - Kinetic plots for the adsorption of dye onto Na-Bt. 1: Telon-Orange, 2: Telon-Red, 3: Telon-Blue

The coefficients values of the pseudo-first order model (≥0.98) were better than those of the pseudo-second order model for the adsorption of dyes at the considered concentration, suggesting that pseudo-first order model was more suitable to describe the adsorption kinetics of dyes onto Na-Bt.

3.2. *Adsorption on Organo-Bt*

The type of bisimidazolium cation and dye to be retained played key roles, inasmuch as maximum dye amounts of 108.3 (for Telon-orange), 96.7 (for Telon-red) and 82.4 mg/g (for Telon-blue) were adsorbed of p-MBIM–Bt, while the lowest were obtained when using o-MBIM–Bt. Compared to Na-Bt (the maximum dye retention level did not exceed 27.8 mg/g), the use of organo-Bt for dyes adsorption is more favourable.

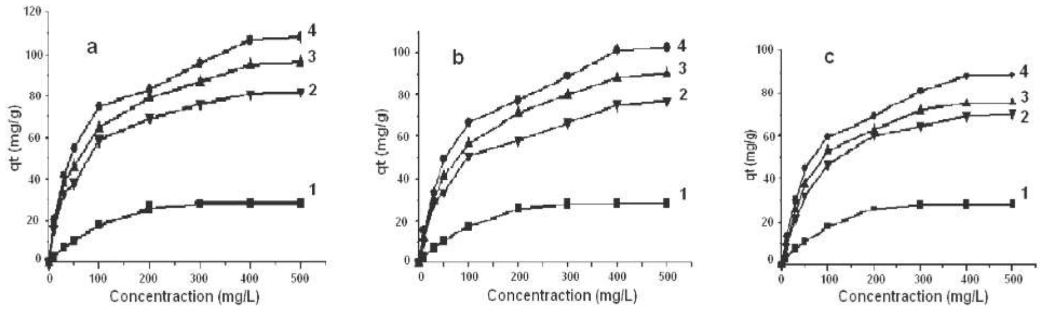

Fig. 4 - Amount of adsorbed dye on organo-Bt. a: Telon-Orange, b: Telon-Red, c: Telon-Blue.
1: Na-Bt, 2: o-MBIM–Bt, 3: m-MBIM–Bt, 4: p-MBIM–Bt

3.3. *Dye Adsorption modeling*

A first approach to describe the adsorption process was achieved with Langmuir's model, by plotting (C_e/q_e versus C_e). Satisfactory linearity was obtained, and the (R^2) values reached 0.98 for the adsorption of Telon-blue onto (o, m, p)-MBIM–Bt (Table 4). The values between 68.44 to 88.45 mg/g for the amount of an adsorbed dye monolayer (q_m) were in agreement with the respective maximum amounts of dye adsorbed (q_{max}) onto these organo-Bt, namely 68.44 (o-MBIM–Bt), 83.53 (m-MBIM–Bt) and 88.45 mg/g (p-MBIM–Bt). Adsorption of Telon-orange and Telon-red did not correlate with Langmuir's model. The specific behaviour of Telon-blue must be due to its higher molecule length and its higher number of sulfonate groups.

Table 1 - Langmuir parameters for dyes adsorption onto organo-Bt

ɔrbent	p-MBIM–Bt		m-MBIM–Bt		o-MBIM–Bt	
elon	ng/g)	/g)	ng/g)	/g)	ng/g)	/g)
ange	3.23	1	5.16	)8	.48	)9
Red	2.57	8	.47	1	.45	4
lue	.45	3	.53	3	.44	4

In most cases of dyes adsorption onto organo-Bt, Freundlich model turned out to be more adequate, inasmuch as the (R^2) values were highly significant, being closer to unity than those obtained in Langmuir's approach (Table 5).

Table 2 - Freundlich parameters for dyes adsorption onto organo-Bt

t	p-MBIM–Bt			m-MBIM–Bt			o-MBIM–Bt		
		F							
	24	71	)9	73	49	)9	29	02	)9
	68	49	)8	20	96	)8	81	)2	)8
	72	43	)8	50	73	)8	17	36	)8

Better linearity was observed for all isotherms in the whole range of concentration investigated, when plotting ln(q_e) as a function of ln(C_e). This was presumably due to heterogeneity of the organo-Bt surface and to dyes–adsorbent interactions. The latter may strongly depend on the chemical structure of the dye molecules.

CONCLUSION

The research was carried out in this paper clearly suggests that bisimidazolium modified bentonite acts a well adsorbent for the removal of Telon dyes from aqueous solutions.

Preparations of new organo-Bt were carried out through the intercalations of bisimidazolium cations into purified bentonite. The surface modification of organo-Bt was examined by using various technique; measurement of the d-spacing of the (001) peak indicate that about (3–7 Å) increase in basal spacing was due to the introduction of organic cations into the bentonite interlayer.

Batch studies applied to Telon dyes revealed a significant increase of the maximum adsorption capacity from 21-28 on Na-Bt to 88-108 $mg.g^{-1}$ on organo-Bt. Physical adsorption may take place on Na-Bt, but stronger dye-adsorbent interactions and anion exchange on positively charged edge sites must also be involved in Telon-dyes retention on organo-Bt. The highest adsorption capacity was noticed for Telon-orange dye on the p-MMBI–Bt, presumably due higher interlayer space and better diffusion.

The pseudo-first order rate equation was able to provide the best description of adsorption kinetics data for all three dyestuffs. Also, a pseudo-second order kinetic and intraparticle diffusion models have been applied to predict the rate constants of adsorption and equilibrium adsorption capacities. The straight lines obtained for the Langmuir and Freundlich models obey to fit well with the experimental equilibrium data but the Freundlich model gives slightly better fitting than Langmuir model.

The results show that bisimidazolium modified bentonite could be employed as low-cost material for the removal of Telon dyes from effluents.

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