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Journal International Sciences et Technique de l'Eau et de l'Environnement,
Vol. (viii), No.3, Decembre 2023, pp.13-16
ISSN Online: 1737-9350; ISSN Print: 1737-6688, Open Access
www.jiste.org
Scientific Press International Limited
Received: Received: 10 June 2023 / Revised: 13 August 2023 / Accepted: October 2023/ Published: December 2023

Adsorption de colorants Anthraquinoniques hydro soluble par une bentonite naturelle

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Résumé

Le but de ce travail était d'étudier l'adsorption de colorants textiles synthétiques (Bezathren-Bleu, Bezathren-Vert et Bezathren-Rouge) par une bentonite sodique (Bt-Na+). Des expériences d'adsorption ont été réalisées selon un procédé discontinu pour évaluer la performance de notre bentonite dans l'adsorption des colorants Bezathren. Plusieurs paramètres ont été étudiés, par exemple : la concentration initiale de colorants, le pH de la solution, le temps de contact et la température. Selon les résultats, l'absorption des colorants Bezathren par Bt-Na+ était rapide et les meilleurs rendements ont été obtenus à pH faible. Les capacités d'absorption maximales (qm) pour Bezathren-Bleu, Bezathren-Vert et Bezathren-Rouge étaient respectivement de 35,08 mg.g-1, 32,88 et 48,52 mg.g-1. Différents types d'isothermes d'adsorption et de modèles cinétiques ont été utilisés pour décrire le comportement d'adsorption des colorants. Les résultats suggèrent que notre bentonite convient comme matériau adsorbant pour la récupération des colorants Bezathren à partir de solutions aqueuses.

Key Words*:* Bentonite, Colorants textiles, Adsorption, Cénitique, Isotherme

Adsorption of Anthraquinones dyes onto Natural Bentonite from aqueous solutions

Abstract

The aim of the present work was to investigate the adsorption of synthetic textile dyes, such as Bezathren-Blue, Bezathren-Green and Bezathren-Red onto sodium bentonite (Bt-Na+). Adsorption experiments were performed under batch process, to assess the performance of Bt-Na+ for the removal of Bezathren-dyes, using initial dyes concentrations, pH of solution, contact time and temperature as variables. According to results, the uptake of Bezathren-dyes by Bt-Na+ was rapid and the maximum sorption was observed at lowest pH. The maximum uptake capacities (qm) for Bezathren-Blue, Bezathren-Green and Bezathren-Red were 35.08 mg.g-1, 32.88 and 48.52 mg.g-1 respectively. Different types of adsorption isotherms and kinetic models were used to describe the Bezathren-dyes adsorption behavior. The results suggested that Bt-Na+ is suitable as a sorbent material for recovery and adsorption of Bezathren dyes from aqueous solutions.

Mots clés: Bentonite, Dyes, Isotherms, Kinetic, Adsorption, Waste-water

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1. INTRODUCTION

Industrial waste water contains many contaminating organic and inorganic materials, such as aromatic compounds, heavy metals and dyes. Colored dyes are important water pollutants which are generally present in the effluents of the textile, leather, printing, laundry, tannery, rubber, plastic, painting and other industries [1]. The presence of very low concentrations of these dyes generates colored wastewater which produces toxicological and technical problems and environmental pollution [2]. Untreated disposal of this colored water into receiving water body causes severe damages to human bodies and to aquatic life [3].
The 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 [4]. However, all these conventional methods have some disadvantages such as high consumption of reagent and energy, low selectivity, high operational cost and generation of secondary pollutants [5]. In contrast, adsorption could be the most cost-effective for metal removal due to easy operation, high efficiency over a wide concentration range and low secondary pollution with suitable regeneration operation.
Bentonite is the clay mineral that was chosen for this study. It is clay mainly composed of montmorillonite which is a 2:1 type aluminosilicate, that is, its crystalline structure presents an alumina octahedral layer between two tetrahedral layers of silica which, by isomorphous substitutions, require cations, denominated exchange cations, to compensate the negative charges of their laminar edges. Bentonite has the capacity to exchange these cations with the ones present in aqueous solutions of organic or inorganic salts. This property is mainly responsible for the great adsorbent power of bentonite, especially toward ions in solution.
The aim of the present work is to investigate the possibility of Bt-Na^+ as an adsorbent for removal of Bezathren dyes, which is, namely Red, Blue and Green, from aqueous solution by adsorption. Effects of pH and temperature on the adsorption process are also investigated. The adsorption capacity of Bezathren dyes with Bt-Na^+ was carried out using two kinetic models, which are the pseudo-second order and pseudo-first order. Finally, the experimental data were compared using two isotherm equations, 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 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, 13.0% loss on ignition at 950°C. The mineralogical analysis showed that the native crude clay mineral contains preponderantly Montmorillonite (86 wt.%); The clay composition also includes Quartz (10%), Cristoballite (3.0%) and Beidellite (less than 1%) [6].
The cation-exchange capacity (CEC) of bentonites was determined according to the ammonium acetate saturation method and was found to be 70 meq per 100 g of dry natural-Bt and 98 meq per 100 g of dry Bt-Na^+ [7]. The BET specific surface area increase from 50 m^2/g in natural-Bt to 95 m^2/g in Bt-Na^+.

2.2. Adsorption and procedure

The method of adsorption used for this study, was carried out by a mixture of 10 mL of Blue and Green dyes solutions of known concentration (C_0=50 ppm), and 0.05 g of our Bt-Na^+ and 15 mL of Red dye solution with 0.03 of Bt-Na^+ in Erlenmeyer with stopper, under vigorous stirring (700 rpm) at room temperature (20±2°C). Both liquid and solid phases were separated by centrifugation; the liquid phase was measured by the UV-visible spectrometer. These compounds absorbed at wavelength (λ_{max}) 600.0 nm for Bezathren-Bleu, 630.0 nm for Bezathren-Green and 510.4 nm for Red. The amount of adsorbed dyes at equilibrium times (q_t, mg/g) was calculated using following relationship:

$$q_t(mg/g) = \frac{c_i - c_t}{W} \times V \quad (1)$$

The percentage removal of dyes was calculated by the following equation. (Eq. 2):

$$Adsorption\,(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Where C_i, C_t and C_e (mg/L) are the initial, time t and equilibrium dyes concentrations, respectively; V and W are the liquid volume (L) and the weight of dried used adsorbent (g).

3. RESULTS AND DISCUSSION

3. 1. Characteristic results of Bt-Na⁺

The IR spectrum of Bt-Na⁺ (Fig. 1) reveal the presence of characteristic absorption bands of clay such as bands corresponds to Si-O, Si-O-M, and M-O-H (M = Al, Fe or Mg) existing between anions and cations located in octahedral and tetrahedral sheets, and OH groups. For example, bands between (3620-3640 cm^{-1}) can be associated to stretching vibrations of O–H groups coordinated to Al and Mg atoms (3640 cm^{-1}) or two Al atoms (3620 cm^{-1}) in octahedral sheets of bentonite; For the band centered at 1027 cm^{-1}, it characterizes the Si–O stretching vibrations; The stretching vibrations bands of Si–O–M^{VI} (M= Al, Mg, and Fe) located in octahedral sheets appears at 400-550 cm^{-1} range [8,9]. For M^{VI}–OH bands (M^{VI} = Al, Mg, et Fe): Al^{VI}–OH vibrations occur at 920 cm^{-1}, sharing of the OH group between Fe and Al in octahedral sheets can move this peak until about 815-915 cm^{-1}, in the case of our sample of Bt-Na⁺, the peak appears at 913 cm^{-1}. 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 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 was found to be 14.5 Å and 13.2 Å, respectively.

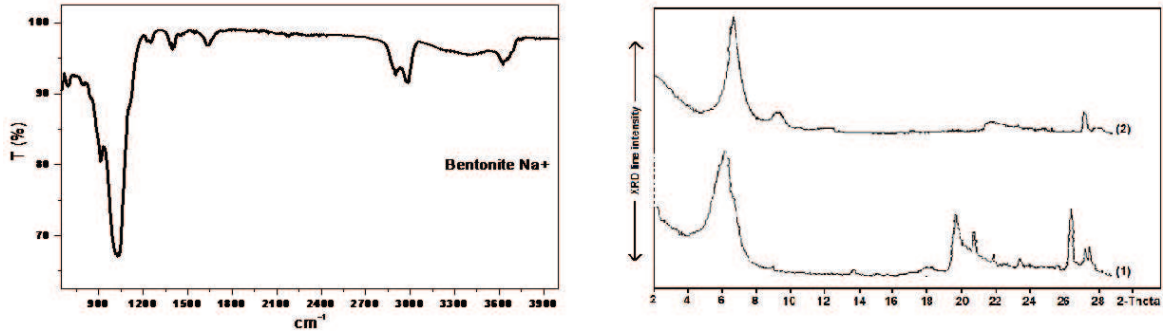

Fig. 1 - FTIR spectrum of Bt-Na⁺ and XRD patterns for bentonites before (1) and after (2) purification

3.2. *Dye adsorption over Bt-Na⁺*

The kinetic of adsorption that describes the solute uptake rate governing the residence time of the sorption reaction is one of the important characteristics that define the efficiency of sorption. The adsorption of dyes on Bt-Na⁺ was studied as a function of contact time and results are shown in Fig. 2. As seen, the adsorption of dyes increases rapidly with increasing time. The time needed for sodic bentonite to adsorb the maximum of Bezathren-Blue is 15 minutes (47.80%, 5.334 $mg.g^{-1}$) and 45 minutes to adsorb the maximum of Bezathren-Green (29.40%, 2.94 $mg.g^{-1}$) and Bezathren-Red (11.53%, 2.86 $mg.g^{-1}$), and then tended to keep constant after this time.

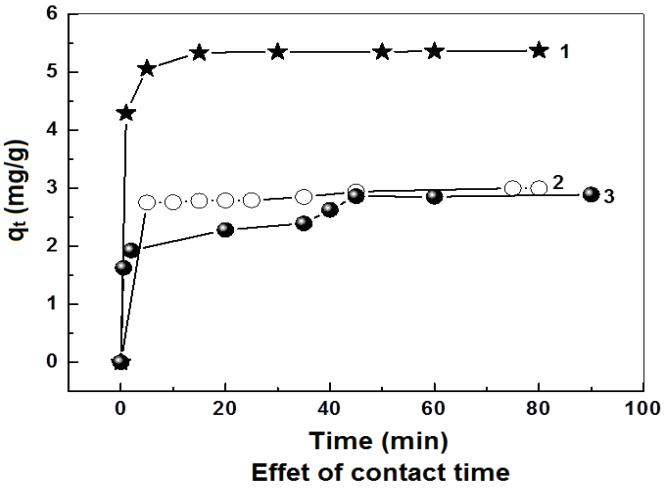

Fig. 2 - Adsorption of Bezathren-Dyes onto Bt-Na⁺ (1: Blue dye; 2: Green dye; 3: Red dye)

In an attempt to express the mechanism of dyes adsorption onto the Bt-Na^+, the pseudo-first order model (PFO) and pseudo-second order model (PSO) kinetic model equations are used to analyze the adsorption experimental data for determination of the related kinetic parameters. The values of rate constants and correlation coefficients for each model were shown in Table 1. It was observed that the pseudo-second order model agreed with the experimental data better than the pseudo-first order model for the adsorption of dyes, High correlation coefficients are obtained when employing the pseudo-second order model ($R^2 \geq 0.9995$) and the calculated equilibrium sorption capacity is similar to the experimental data, and this indicated that the adsorption of Bezathren-dyes onto Bt-Na^+ is controlled by chemical adsorption (chemisorption) involving valence forces through sharing or exchange electrons between sorbent and sorbate. In chemical adsorption, it is assumed that the adsorption capacity is proportional to the number of active sites occupied on the adsorbent surface.

Table 1 - Pseudo-first order and pseudo-second order models for adsorption onto Bt-Na^+

	q_e (exp.)	Pseudo-first order	Pseudo-second order
Bezathren-Blue	5.33 $mg.g^{-1}$	$R^2 = 0.854$ $q_e(calc) = 3.249\ mg.g^{-1}$ $K_1=5.194\ min^{-1}$	$R^2 = 0.999$ $q_e(calc)= 5.385 mg.g^{-1}$ $K_2=0.761\ min^{-1}$
Bezathren-Green	2.94 $mg.g^{-1}$	$R^2 = 0.527$ $q_e(calc) = 0.675\ mg.g^{-1}$ $K_1=0.0685\ min^{-1}$	$R^2 = 0.999$ $q_e(calc)= 3.039\ mg.g^{-1}$ $K_2=0.225\ min^{-1}$
Bezathren-Red	2.86 $mg.g^{-1}$	$R^2 = 0.802$ $q_e(calc) = 1.542\ mg.g^{-1}$ $K_1=0.042\ min^{-1}$	$R^2 = 0.999$ $q_e(calc)= 2.942\ mg.g^{-1}$ $K_2=0.108\ min^{-1}$

CONCLUSION

The research carried out in this study showed that Bt-Na^+ is effective adsorbent for the removal and recovery of Bezathren-dyes from aqueous solutions. The adsorption of Bezathren-Blue reaches equilibrium within 15 min and 45 min for both Bezathren-Green and Bezathren-Red. The optimum pH for the effective adsorption of dyes was founded as 1.4 for Bezathren-Red, 1.5 for Bezathren-Green and 2.35 for Bezathren-Blue. The adsorption equilibrium follows Freundlich isotherms model and the maximum adsorption capacities were calculated to be 35.08 $mg.g^{-1}$, 32.88 and 48.52 $mg.g^{-1}$ for Bezathren-Blue, Bezathren-Green and Bezathren-Red respectively. The adsorption kinetics followed the pseudo-second order kinetic model for all three dyestuffs. The results show that sodic bentonite could be employed as low-cost material for the removal of bezathren dyes from effluents.

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