

Altering Bentonite Through Acid Treatment: The Use of Rhodamine B in Water Purification

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Abstract

Natural bentonite is an adsorbent that can be easily modified to become a promising adsorbent for the removal of organic and inorganic effluents. In this present work, the natural bentonite of the M'Zila deposit (Mostaganem) was activated with sulfuric acid in order to increase the specific surface and the porosity of this material. The modifications made to the bentonite after its activation were highlighted by BET, X-ray fluorescence as well as the cation exchange capacity. The results found showed that for a low concentration of the acid solution (1N) and at different periods of agitation of the suspension (bentonite / acid), the specific surface area increases with increasing contact time. The results of the elemental chemical analysis obtained by X-ray fluorescence showed the increase in the atomic percentage of sulfur after treatment which was initially 0.28% and that the variation in the atomic percentage of sulfur increases as well with the increase in concentration. acid only with the bentonite / acid solution contact time. In addition, the C.E.C of the four adsorbents obtained after treatment is greatly influenced by the concentration of the acid solution. Natural and treated bentonite was used for the adsorption of Rhodamine B (RhB), the effects of various experimental parameters, such as the initial adsorbent concentration, and the contact time between adsorbent and adsorbate, have been studied.

Keywords: Bentonite, Rhodamine B, Sulfuric Acid, Chemical Activation, Adsorption

Introduction

Nowadays, pollution is one of the most serious environmental problems, for which greater concern for the conservation of natural resources as well as the protection of the biosphere, is due to human activity. Most of the pollutants are very toxic and non-biodegradable organic compounds, which are introduced into river waters by pollution brought by urban areas, and the discharge of effluents from certain industries. Furthermore, these compounds pose a health risk and must be eliminated.

Wastewater from the textile industry poses considerable environmental problems worldwide. In particular, water containing soluble dyes which must be cleaned before being discharged into nature. Rhodamine B (RhB) dye is a synthetic dye widely used as a dye in the manufacture of textiles and food products. He was medically proven that drinking water contaminated with

rhodamine-based dyes can lead to subcutaneous tissue-borne sarcoma which is highly carcinogenic [1].

Various treatment methods have been used to remove the different types of pollutants present in wastewater, such as electrochemical degradation, electrocoagulation, membrane processes, and adsorption [2-5]. However, their implementation remains expensive, as for adsorption processes, activated carbon is one of the most commonly used adsorbents to remove organic and inorganic pollutants from wastewater. Although activated carbon has a high adsorption capacity, due to its high specific surface area, it is an expensive adsorbent material.

In contrast, clays are abundantly available in nature and are inexpensive materials that exhibit high adsorption capacity and can be modified with organic and/or inorganic substituents. Benton-

ite is a natural clay belonging to the group of smectites, is essentially made up of montmorillonite [6]. Bentonite is considered the main candidate for environmental remediation of wastewater contaminated with toxic compounds due to its lack of toxicity, high specific surface area, cation exchange capacity, hydration, its swelling and the presence of active adsorption sites and its hydrophilicity which allow easy fixation of biomolecules and adsorption of a wide variety of substances [7]. However, these materials must be treated before application to modify their interaction [8].

In Algeria, the most economically important bentonite deposits are found in Oranie (Western Algeria). We note in particular the quarry of Maghnia (Hamman Boughrara) whose reserves are estimated at one million tons and that of Mostaganem (M'Zila) with reserves of two million tons. Bentonite is considered a prime candidate for the remediation of the environment contaminated by wastewater.

The purposes of this work are: to study the influences of the concentration of sulfuric acid and the bentonite-acid contact time on the properties of bentonite. In addition, the elimination of RhB in an aqueous solution by chemically treated bentonite.

Adsorbent Preparations

A mass of 20 g of bentonite is brought into contact with 250 mL of sulfuric acid solution with magnetic stirring for a well-defined period of time. The mixture is brought to reflux for a temperature of 90 °C, which is controlled by a thermometer immersed in the solution. The temperature is kept constant throughout the activation process by means of a water bath. The contact time between clay and acid is 1 and 3 hours, which was determined from the moment when the temperature of the suspension reaches 90 °C, and the concentration of the acid is 1 N and 2 N. Each time the treated bentonite is filtered then washed several times with dis-

tilled water, to remove excess acid, before being dried in an oven overnight at 105 °C and then ground and sieved.

The adsorbents obtained are: AC-1-1, AC-1-2, AC-3-1, AC-3-2,

Adsorption Method

A stock solution of Rhodamine B was prepared by dissolving 1 g in 100 ml of distilled water. The adsorbed quantities were determined by measuring their characteristic UV-Vis absorbance at a maximum wavelength of 555 nm.

Effect of the adsorbate/adsorbent contact time: Suspensions are stirred continuously in glass tubes, a mass of 1 g/L of adsorbent is dispersed in 10 ml of the RhB solution with an initial concentration of 20 mg/L. After a well-defined contact time, the adsorbent is separated by centrifugation.

Effect of adsorbate concentration: The adsorption protocol used is exactly the same as for the effect of adsorbent concentration. The range of concentrations used for Rh B solutions is 5 to 25 mg/L and the mass of the adsorbent is 1 g/L.

Results

Characterization of Adsorbents

Surface Analysis by Adsorption-desorption of Nitrogen (B.E.T): The results of the specific surface of the chemically treated bentonite are given in Table 1. Considering the experimental parameters, it is found that the specific surface increases with the increase of contact time with 1 N acid concentration, the greatest is observed with AC-3-1, but unlike the surface area decreases for a long period of treatment with 2 N acid concentration, the lowest of four adsorbents is observed with AC-3-2. Compared to the parent adsorbent (bent), the specific surface area increases for all adsorbents. acid treatment of bentonite creates a charge deficiency in the bentonite due to removal of Al^{3+} and Mg^{2+} . Thus, the increase in the surface of the pores [8].

Table 1: Specific Surface and Pore Width of Bentonite Treated with H₂SO₄

Adsorbants	2 S (m ² /g) BET	Largeur des pores (Å)	Volume des pores (cm ³ /g)
bent	38.36	159.37	0.109
AC-1-1	73.77	161.66	0.140
AC-3-1	79.76	170.15	0.167
AC-1-2	59.27	167.80	0.139
AC-3-2	54.80	135.36	0.136
AC-1-2	59.27	167.80	0.139
AC-3-2	54.80	135.36	0.136

Characterization by Fluorescence-X: The results in table 2 showed the increase in the atomic percentage of sulfur after bent/acid treatment. For the interlayer (Na^{+} , K^{+} and Ca^{2+}) and structural (Al^{3+} , Fe^{2+} and Mg^{2+}) cations, their atomic percentage gradually decreases with the increase in the concentration of the acid solution and which reflect the progressive dissolution

of the octahedral layer. The results also show an increase in the atomic percentage of silica which increased with a concentration of 2 N of acid and a treatment time of 3 h which increased from 51.62% (bent) to 79.28% (AC-3-2). Similar results have been observed in the literature, where the Si/Al ratio increases with increasing acid treatment time [9].

Table 2: Elemental Chemical Analysis Obtained by X-ray Fluorescence of Bentonite Treated with H₂SO₄ at 90°C

Elements	Elements (% Massive)								
	SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	K ₂ O	MgO	Fe ₂ O ₃	TiO ₂	SO ₃
bent	51.62	13.14	9.36	11.78	3.68	3.05	5.64	0.53	0.31

AC-1-1	64.43	13.08	3.07	6.96	2.34	2.24	4.28	0.50	2.65
AC-3-1	72.28	11.41	0.73	1.34	1.1	2	3.35	0.30	7.24
AC-1-2	74.51	10.33	0.03	1.04	1.04	1.85	3.01	0.18	7.28
AC-3-2	79.28	8.59	0.02	0.69	0.43	0.5	1.66	0.10	8.5

Cation Exchange Capacity (C.E.C): According to the results, for a concentration of H₂SO₄ equal to 1 N and for a contact time of 1 h (AC-1-1) and 3 h (AC-3-1), or for a concentration of 2 N and for a contact time of 1 h (AC-1-2) and 3 h (AC-3-2) the CEC goes from 72.85 to 74.04 meq/100g and from 64.92 to 60.58 meq/100g, respectively. Whereas for the same contact time and with an increase in the concentration of the acid solution, there is a large decrease in the C.E.C. This decrease is attributed to the elimination of interfoliar cations (Na⁺, K⁺ and Ca²⁺) with a low concentration of acid, whereas for a high concentration the attack can arrive until the progressive dissolution of the octahedral layer by gradually decreasing the percentage of structural cations (Al³⁺, Fe²⁺ and Mg²⁺) and which is confirmed by X-ray fluorescence.

Adsorption of Rhodamine B (RhB)

Figures 1 and 2 depict the effect of adsorbent-adsorbate contact time and the effect of initial RhB concentration, respectively. Fig 1 reveals that RhB adsorption equilibrium is reached after 30 min of contact. The q_t (mg/g) is higher with adsorbent A-3-1 and AC-1-1, followed by AC-1-2 and bent, but very low with AC-3-2 and the maximum values reached are 19.48 mg/g, 18.82 mg/g, 17.72 mg/g, 17.00 mg/g and 12.02 mg/g, respectively. The results (Fig 2) showed that q_e (mg/g) of RhB dye by the studied adsorbents increases with increasing initial concentration of RhB. Indeed the maximum adsorption for an initial concentration of 25 mg/L of RhB for AC-3-1, AC-1-1, AC-1-2, AC-3-2 and bent are 22.86, 21.07, 18.75, 13.81 and 17.89 mg/g, respectively.

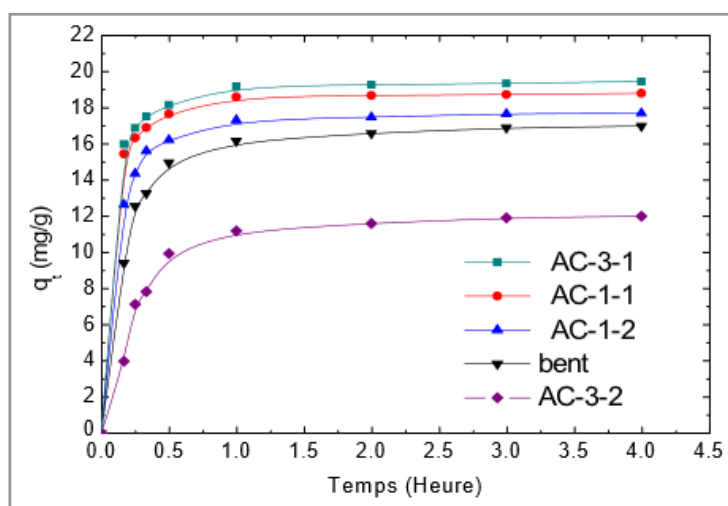


Figure 1: Optimization of Adsorbate-adsorbent Contact Time, $C_i = 20$ mg/L.

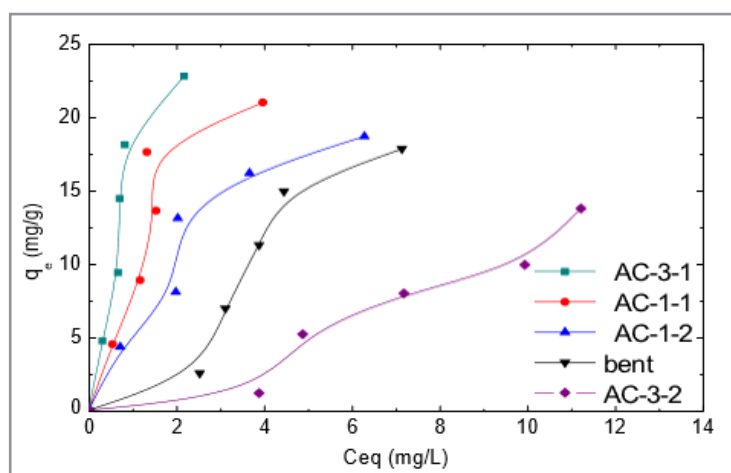


Figure 2: Effect of Initial RhB dye Concentration, $C_e = 5-25$ mg/L

Conclusion

Acid treatment of bentonite increases the specific surface either with increase in bent-acid contact time or increase in acid concentration, but the most important is with 1N and 3 hours (AC-3-1) and there is a partial change in structure for higher acid concentrations. The acid treatment consists in extracting part of the cations in the interlayer space, the Oct layers and the Td layers. Hence there is a replacement of interfoliar cations by protons which leads to a drop in the C.E.C. rhodamine B adsorbs well on bentonite treated with a 1 N sulfuric acid solution with a contact time of 3 hours (AC-3-1). It can be said that the bentonite from Mostaganem has proven to be a promising material for the modification and remediation of water contaminated by dyes.

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