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Removal of a textile dye by pillared clay

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Abstract:

The aim of this work is the preparation of the sorbents based on the modified bentonites and try to elimate the dyes wasteswater by these materials. The dyes used in this study are yellow bemacid E-4G acid and reactive yellow procion MX-4R. The bentonite provide from Mostaganem deposit (Algeria) was added to pillaring solution based on hydroxy-aluminium cations during 4 and 24h, in order to obtain the samples Al-B-4 and Al-B-24. The experimental adsorption data were analyzed by Langmuir and Freundlich isotherms and Pseudo-kinetic models. The results revealed that Freundlich isotherm provided a better fit to the experimental data. The adsorption kinetics followed both the pseudo first and second-order rate equations, while the second order giving a better fit. The Al-bentonite demonstrated the highest adsorption capacity by removing over 95% of E-4G and MX-4R.

Keywords: Bentonite; intercalation; dye; adsorption.

1. Introduction

The clays in general and bentonites in particular are widely used in many industrial applications like, drilling, foundry, ceramics, paint, pharmaceuticals, cement, and paper industries. The bentonites can also be used as an adsorbent to remove various organic or inorganic pollutants in the aqueous solution [1, 2].
Despite significant physicochemical properties that have this type of clay, they can be substantially improved by a structural change inserting of the pillars such as hydroxy-aluminium cations [3, 4]. The pillaring of the clay lies in the intercalation of metal poly-cations between the sheets in order to obtain microporous materials with rigid structure and a large interlayer spacing [5].
Recently the synthetic dyes are consumed broadly in textile industries and large volumes of dye wastewater are produced. It is estimate at 10,000 are discharged annually and around 50% of all dyes are azo dyes [6]. To this environmental problem, we suggest the application of the modified bentonite to adsorb the dye wastewater.
In this study we used an original Mostaganem bentonite (western Algeria) as adsorbent to remove dyes from the textile industry. Two applied dye are yellow bemacid E-4G acid and reactive yellow procion MX-4R. Several analytical techniques were used to identify the samples before and after treatment, such as XRD, BET, chemical composition, etc. The preparation of the sorbent samples was made by bentonite purification, followed by an intercalation of hydroxy-aluminum species. The adsorption of dyes by pillared bentonite was carried out by the isotherms construction, the fitting adsorption data by Langmuir and Freundlich equations and kinetic study.

2. Materials and Methods

2.1. Starting materials

The bentonite used for this study was purchased from M'zila deposit (Mostaganem city, Algeria). Before the experiments, the samples were purified and sieved at 80 µm.NaCl, $AlCl_3$, $AgNO_3$, NaOH and HCl were all of analytical grade, obtained from Aldrich.

2.2. Preparation of pillaring solutions

The pillaring solution of hydroxy-aluminum cations ($[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$) was prepared by adding 0.2 mol/L of NaOH solution to 0.2 mol/L of $AlCl_3$ solution under vigorous stirring at 60°C, until ratio molar OH^-/Al^{3+} reached 2. The solution was stored at room temperature for three days before using.

2.3. Preparation of pillared bentonite

The resulting pillaring solutions were added to bentonite by stirring for 04 and 24h at 70 °C at the ratio of 50 mmololigomericcations per gram of Bentonite. The slurry was stirred for 24 h at room temperature, filtered, and washed repeatedly with deionized water until there was no chloride, verified by the $AgNO_3$ test. The solid was dried at 80 °C and kept in a sealed bottle. The two inorganic pillared bentonites were designated as Al-B-4 and Al-B-24 respectively.

2.4. Adsorbates

Bemacid Yellow E-4G and Procion Yellow MX-4R were provided by the SOITEX textile society (Tlemcen, Algeria). Synthetic test dyes solutions were prepared by dissolving accurately weighed amounts of dye (1 g/L) in distilled water and subsequently diluted to required concentrations. The chemical formula of B.Y E-4G and P.Y MX-4R are $C_{16}H_{13}Cl_2N_5O_3S$ and $C_{20}H_{19}ClN_4Na_2O_{11}S_3$ respectively.

2.5. Characterization methods

The chemical analysis of natural bentonite was performed with X-fluorescence. X-ray analysis were performed using INEL CPS 120 diffractometer employing cobalt Kα radiation (λ= 0.178 nm). The specific surface area and porosity data were determined by adsorption of nitrogen via a Quantachrome instrument. Residual concentrations of dyes were detected using UV-vis spectrophotometer (VIS 7220 G, Biotech Engineering Management).

2.6. Batch Experimental Procedure

Batch experiments were carried out by mixing 20 mL of known concentration of MX-4R and YB E-4G solutions with 0.1 g of Al-Ben. The mixtures were then agitated at room temperature. Various parameters such as effect of contact time (10–150 mins), effect of medium pH (1–7), and effect of temperature (20, 30, 40, and 50°C) were done for optimizing the experimental conditions. The medium pH was adjusted using 1 M HCl and 1 M NaOH. The experiments were done under agitation time of 3h, determined from the effect of contact time experiment, after which the mixtures were filtered and the filtrates were analyzed for MX-4R and E-4G content using UV-Vis at wavelength of 425 and 400 nm, respectively. The amount of dye adsorbed per gram of Al-Ben, (mg/g), was calculated using:

$$q_e = \frac{(C_0 - C_e)}{m} V \quad (1)$$

where $C_0$is the initial dye concentration (mg/L), C_e is the equilibrium dye concentration (mg/L), V is the volume of dye solution used (L), and m is the mass of material used (g).

3. Results and discussions

3.1. Characterisation of the materials

From the elements analysis result, the chemical composition of natural bentonite is follows: 64.22% SiO_2, 11.62% Al_2O_3, 9.33% CaO, 4.88% Fe_2O_3, 3.47% MgO, 3.38% Na_2O, 1.06% TiO_2, 0.46% SO_3, 0.03% P_2O_5 and loss of ignition 1.55%. The Silica, alumina and lime are the major oxides in our sample and the trace elements such as iron, magnesium, sodium, titanium, sulphate and phosphor oxides are considered as impurities.

X-ray diffraction patterns of the samples are illustrated in Fig. 1. X-ray diffractogram of the Ben-N showed an intense d_{001} peak at 8.07, corresponding to a basal spacing of 1.27nm. After hydroxy-aluminum polycations exchange Al-B-4 and Al-B-24, the d_{001} value increased to 1.36 and 1.43 nm, respectively. The (001) peaks of Al-B-4 and Al-B-24 were much less intense compared to that of Bentonite natural in agreement with previous results obtained by Yan et al. [7]. The BET surface area of Ben-N was 59.02 m^2/g. After pillaring with Al_{13} the surfaces area of Al-B-4 and Al-B-24 were increased to 110 and 84.4 m^2/g, respectively. The increasing in pillaring Al_{13} time resulted in a slight increase in the basal spacing and a significant increase in the surface area. However, a long time for bentonite pillaring by hydroxy-aluminum cations, is indeterminate to obtain the better results of the surface area and the basal spacing.

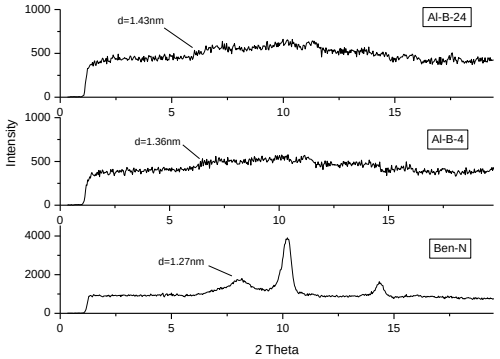

Figure 1. XRD patterns of Ben-N, Al-B-4 and Al-B-24.

3.2. Effect of pH

The amount of E-4G and MX-4R adsorbed onto Ben-N and pillared bentonites at various pH values are illustrated in Fig.2. As presented in Fig. 2a, the amount of E-4G adsorbed is more significant in the pH range of 1-3 for the three samples, and decrease above pH 4. In Fig.2b, the amount adsorbed of MX-4R onto Ben-N is very high at pH 1 and decrease when the pH value increase and the MX-4R adsorption become inexistent near the neutral pH. While for Al-B-4 sample MX-4R adsorption increase between pH 1 and 4, above this pH value, the amount adsorbed decrease.

Since E-4G and MX-4R are anionic dyesadsorbed by the sample sofbentonite, whichdevelop a positive surfacechargesinthe acidic medium. So the bestamountadsorbed of bothdyeswillbe at pHweak, whenelectric chargesare opposite signbetweensorbent and adsorbate [8, 9].

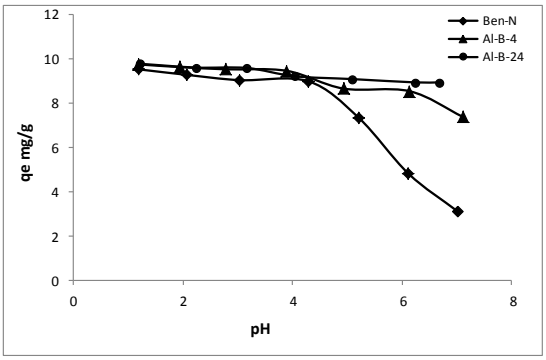

Figure 2a. Effect of pH on E-4G adsorption onto Ben-N, Al-B-4 and Al-B-24. E-4G solution concentration 50 mg/L, contact time 3h, adsorbent dose 5 g/L.

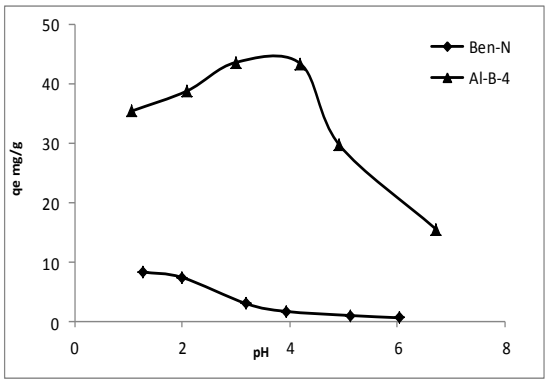

Figure 2b. Effect of pH on MX-4R adsorption onto Ben-N and Al-B-4. MX-4R solution concentration 100 mg/L, contact time 3h, adsorbent dose 5 g/L.

3.3. Adsorption kinetics

The adsorption kinetic data of E-4G and MX-4R were determined by testing pseudo-first order and pseudo-second order kinetic models. The adsorption of the both dyes on the two adsorbents increased with time and reached equilibrium at 60 min (Fig. 3). The adsorption rates of the E-4G and MX-4R by Al-B-4 and Al-B-24 are rapid early in the process and becoming slower over time. When dye concentration was low, adsorption was very fast due to availability of the active sites and less competition. With increasing dye ion concentration, competition for the adsorption sites decreased the adsorption rate [10].

The best agreement was achieved for pseudo-second order equation [11]:

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

where k_2 is the rate constant of the pseudo-second-order model for the adsorption process (g/mg.min). Plots of t/q_t against *t*have been drawn to obtain the rate parameters.

The results obtained are expressed in Table 1. We see that the correlation coefficients of the both pillared bentonites are almost equal to unit. The sorbents Al-B-4 and Al-B-24 adsorbs a same amount of dye.

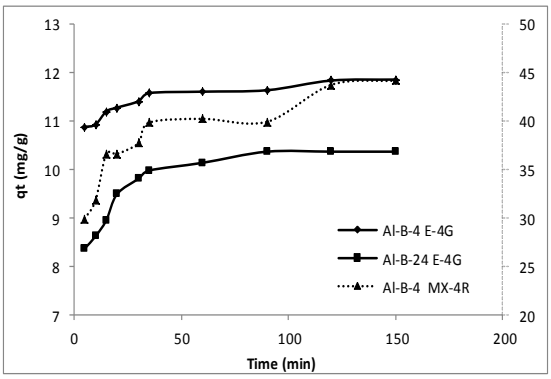

Figure. 3. Effect of contact time on E-4G and MX-4R (dashed line) adsorptions onto Al-B-4 and Al-B-24. ($C_{0\ MX\text{-}4R}$ = 250 mg/L, $C_{0\ E\text{-}4G}$ =60 mg/L, pH= 2-3, adsorbent dose 5 g/L).

Table 1. Constants rate of the adsorption of E-4G and MX-4R by Al-B-4 and Al-B-24

Dye	E-4G			MX-4R		
Model	Pseudo- second order			Pseudo-second order		
	q_e	K_2	R^2	q_e	K_2	R^2
Al-B-4	12.048	0.922	0.999	45.455	0.912	0.997
Al-B-24	11.037	0.474	0.999	39.522	0.463	0.993

q_e: (mg/g), k_2: (g/mg.min)

3.4. Adsorption isotherms

The adsorption isotherms are realised at different initial concentrations during 3h at ambient temperature, adsorbent dose 5g/L and pH 3. The isotherms are formed by plot adsorbed amount of dye versus equilibrium concentration. The figure 4 and 5 presents the adsorption of E-4G and MX-4R by the pillared bentonites, respectively. We see that he amount of dye increase with increasing in equilibrium concentration dye. All isotherms show the S-shap according to the classification of Gile et al. [12]. The S-shap means that the adsorption is cooperative where the adsorbed molecules facilitate the adsorption of the other molecules. We note also there is no difference in adsorbed amount of E-4G between Al-B-4 and Al-B-24 which was 87 mg/g, but the amount adsorbed of E-4G by Al-B-4 is more important than that of MX-4R in same operating conditions.

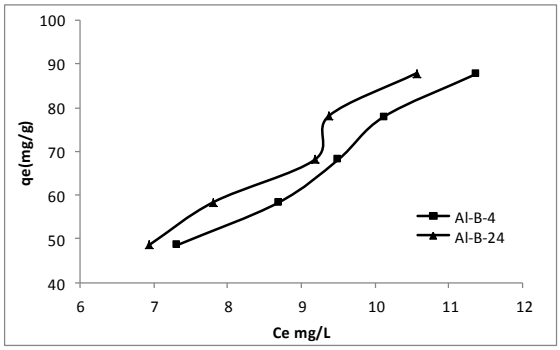

Figure. 4. Isotherms adsorption of E-4G onto Al-B-4 and Al-B-24.

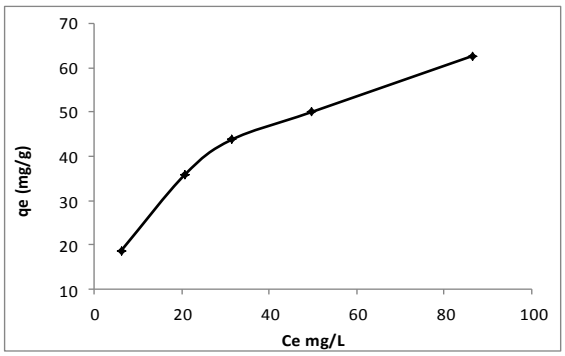

Figure. 5. Isotherm adsorption of MX-4R onto Al-B-4.

Table 2. Isotherms constants

Sample	Al-B-4			Al-B-4			Al-B-24		
model	Langmuir model			Freundlich model			Freundlich model		
	Q_0	K_L	R^2	1/n	K_F	R^2	1/n	K_F	R^2
E-4G	ins	ins	ins	1.396	2.96	0.984	1.398	3.25	0.972
MX-4R	76.92	0.044	0.989	0.455	8.60	0.988			

The Langmuir and Freundlich equations expressed in relations (3) and (4) were used for modeling the adsorption data.

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (3)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

where Q_0 is the maximum adsorption capacity (mg/g), and K_L(L/mg) is Langmuir adsorption constant. K_F and n are the Freundlich constants, indicating the capacity and intensity of adsorption, respectively.

The fitted constants for Langmuir and Freundlich models are summarized in Table 2. The regression coefficients (R^2) values were obtained for Freundlich isotherm were above 0.98, indicating a very good mathematical fit by this model. Except the adsorption of MX-4R by Al-B-4 which was described by the both models. Similar results have been reported for the adsorption of Congo red [13] and reactive Blue 19 [14] by modified bentonite. The constants 1/n were above to the unit in the cases of the adsorption of E-4G by the pillared bentonites, that means the adsorption intensity was weak, but in the case of the adsorption of MX-4R by Al-B-4 the 1/n value was 0.455, that means this adsorption is intense and favourable.

4. Conclusion

Al pillared clays were prepared by direct introduction of Al_{13} pillaring solution into the dilute bentonite suspension during 4 and 24h, and the prepared Al pillared bentonite were used to remove two different textile dyes Y.B E-4G and Y.P MX-4R from aqueous solution.

Upon intercalation the d_{001} spacing increased from 1.27 to 1.43 nm. In addition the surface area of the pillared samples also increased from 59 m^2/g of the pure bentonite to 110 m^2/g. Al pillared bentonites occur as good sorbents for removal of reactive dyes. The amount adsorbed of dye was 87 mg/g in just 60 min. Due to experiment data, there is no significant difference on efficacy between the samples pillared at 4h or 24h. Therefore in these cases it's preferable to economize the time and the energy.

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