



## Wastewater Treatment by Xylene Adsorption Using Pillared Bentonite

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### Abstract

In this paper, the ability of pillared clay by Al/Fe polymerics as an adsorbent for the removal of p-xylene from an aqueous solution has been investigated under various experimental conditions. Bentonite from Hammam Bouhrara located in Maghnia village (Algerian) was purified then, modified by intercalation with  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  polymerics (FeAl/B). The adsorption kinetic study showed that equilibrium could be achieved within 30 min. The maximum adsorption capacities of FeAl/B to p-xylene based on the Langmuir isotherm was 275  $\mu\text{g/g}$  with a higher percentage removal up to 99.97%. The adsorption equilibrium data fitted well by the Langmuir adsorption isotherm model. It was found that FeAl/B had high adsorption capacity for p-xylene due to cation exchange and high surface area 224.3  $\text{m}^2/\text{g}$ . FeAl/B was concluded as a promising and effective adsorbent for the removal of p-xylene from wastewater.

Keywords: Adsorption, Bentonite, Wastewater, Xylene.

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### 1. Introduction

Water was such an important element for our daily life and many manufacturing processes that we must consider and be preserved. So, used water was supposed to be treated and discharged again into rivers, which, this water returns to its natural environment, but unfortunately, the most of the times, this water returns with great amount of organic or inorganic substances than its ordinary concentration or with some pollutants substances added, which, it can lead to water pollution. According to EPA, the minimum allowable xylene of 0.5 ppb in drinking water, but if the levels of xylenes exceed the MCL 10 ppm in drinking water can be leads to water pollution and many health risks. Xylene was aromatic compound and clear liquid with generally a very sweet odor and it most likely enter in drinking water by contamination from industrial discharge. In groundwater contaminated by point emissions, xylene levels of 0.3 to 5.4 mg/L have been reported; levels in uncontaminated groundwater are low ( $<0.1 \mu\text{g/L}$ ) [1]. Xylene levels in approximately 3% of all groundwater-derived public drinking-water systems and 6% of all surface-water-derived drinking-water systems in the USA were greater than  $0.5 \mu\text{g/L}$ , the maximum level being  $5.2 \mu\text{g/L}$  [2]. In Canada, m-xylene was found in seven out of 30 potable water treatment plants at concentrations below  $1 \mu\text{g/L}$  [3]. Concentrations in drinking-water can be increased by the leaching of xylene from the synthetic coating materials commonly used to protect the tanks used for its storage [4]. Xylene has dangerous characteristics to cause nervous system damage and may harm developing fetuses. Among various wastewater treatment methods was adsorption. It was

simple, useful, cheap and an effective technique for removed pollutants substances. Granular or powdered active carbon is the most commonly used adsorbent in wastewater treatment because it has a large specific surface area, although it is high cost. Over several decades, many researchers show their interests in searching for low-cost adsorbents with excellent adsorption characteristics, such as bentonite, they were naturally available and possess unique physiochemical properties. Among these properties, their cationic exchange capacity (CEC) and ability to swell in polar media make clays interesting as raw materials for modification through soft chemistry and intercalation methods. Bentonite clay was from smectites and vermiculites family composed of negatively charged layers which were balanced predominantly by sodium or calcium ions. The negative charge was the result of isomorphous substitution in tetrahedral by silicon ions aluminum or ferric cations by and magnesium or ferrous cations in octahedral sheets. The modification by pillaring involves intercalation of large polyoxocation or polymeric in the interlayer space of the natural clay, which improves thermal and mechanical stability, porosity and surface area, basal spacing and accessibility to its acid sites [5] [6]. This study aims to investigate the impact of adsorption capacity of modified bentonite and pillared bentonite with iron and aluminum polymeric (FeAl/B) on xylene removal from aqueous solution. Several kinetic factors were changed such as concentration, contact time and adsorbent mass.

## 2. Experimental Materials and Methods

### A. Adsorbent

The raw bentonite used in this study from Hammam Boughrara located in Maghnia village (Algerian). The adsorbent was purified for eliminant the organic matter using method CBD (Sodium Citrate, Bicarbonate and Dithionite) [7]. The activated bentonite by sodium used for the preparation of the pillared samples was synthesized by the treatment of the purified bentonite with 1M of NaCl at a mass fraction ratio of 1/150 (w/w) between solid and liquid phases at 313 K for 8 h. After that, the aqueous suspension was centrifuged and filtered, and the solid was washed and dried at 383 K for 7 h, ground and sieved. The measure of CEC has given 0.92 meq/g. The procedure of pillared bentonite with iron (III) and aluminum polymeric is prepared sparely by slow addition of a 0.1 M NaOH to a 0.1 M of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  solution or  $\text{FeCl}_3$  solution under constant stirring until obtaining final ratio  $\text{OH}/\text{Al} = 2.5$ . The solutions were left to rest for one week. The polymeric of Al and Fe were mixed and added to activated bentonite suspension with mass ratio of  $\text{M}^{3+}$  ( $\text{M}^{3+} = \text{Fe}^{3+}, \text{Al}^{3+}$ ) / clay equal 6.25, under constant stirring for 10 h at 333 K. The solid was separated by centrifugation and washed several times and calcinated at 737 K for 3 h. It was named FeAl/B, the measure of CEC has given 0.22 meq/g. Submit your manuscript electronically for review.

### B. Characterization of adsorbent

The Analysis of the chemical composition of adsorbent was obtained by scanning electron microscopy EDX and SEM are used to investigate the morphology of purified and pillared clay using JEOL JSM-6400. X-ray powder diffraction (XRD) patterns of the samples are obtained by using filtered  $\text{CoK}\alpha$  radiation.

### C. Adsorption

Different mass of p-xylene was dissolved in water to make 50-200  $\mu\text{g}/\text{L}$  solutions. Then 0.1grams of pillared bentonite or purified bentonite was added to the aqueous solution and was stirred to the room temperature for 5-180 mn.

Then aqueous solution was centrifuged, then filtered and the resulting filtrate was taken for analyzed with gas chromatography for determining the adsorption capacity.

The adsorption equilibrium data was described by the Langmuir isotherm (Eq 1):

$$q = \frac{q_m bc}{1 + bc} \quad (1)$$

Where  $q$  is the equilibrium adsorbed concentration,  $q_m$  is the saturation capacity,  $c$  is the equilibrium liquid phase concentration,  $b$  is the affinity or Langmuir constant.

The Langmuir isotherm parameters have been calculated from the experimental data by linearization of the equation (2)

$$\frac{1}{q} = \frac{1}{q_m b c} + \frac{1}{q_m} \quad (2)$$

### 3. RESULTS AND DISCUSSION

The chemical composition of the purified bentonite has given in Table 1.

**Table 1.** Chemical composition of purified bentonite

Elements	Weight%
SiO <sub>2</sub>	57.96
Al <sub>2</sub> O <sub>3</sub>	22.05
Fe <sub>2</sub> O <sub>3</sub>	2.83
CaO	8.49
MgO	2.37
Na <sub>2</sub> O	2.34
K <sub>2</sub> O	2.84
TiO <sub>2</sub>	1.12
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2.62

It was seen from table that the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were the major elements of bentonite, which ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of this adsorbent was about 2.62 confirmed that montmorillonite is major compose in size particle <2μm.

The comparison of the data obtained for the AlFe/B with those of B in Table 2 showed that an increase in basal spacing ( $d_{001}$ ) was accompanied by increase of BET surface area, which indicated that Fe or Al was occupied the interlayer area. The BET surface area of purified bentonite was 100 m<sup>2</sup>/g, but it increased to 224.3 m<sup>2</sup>/g after pillaring with polymeric AlFe accompanied to high porosity than B clay. The Table 2 showed a progressive increase in basal spacing ( $d_{001}$ ) depending the nature of the polycations intercalated. The  $d_{001}$  was increased from 14,5 Å for B at to 18,02 Å FeAl/B, that confirm that the pillaring process was proven as successful.

**Table 2.** Textural properties and basal spacing of the adsorbent

	<b>B</b>	<b>FeAl/B</b>
<b>pH</b>	8.81	10.02
<b>S<sub>BET</sub> (m<sup>2</sup>/g)</b>	100.2	224.3
<b>Total pore volume (cm<sup>3</sup>/g)</b>	0.12	0.23
<b>Micropore volume (cm<sup>3</sup>/g)</b>	0.04	0.18
<b>d<sub>001</sub> (Å)</b>	14.5	18.02

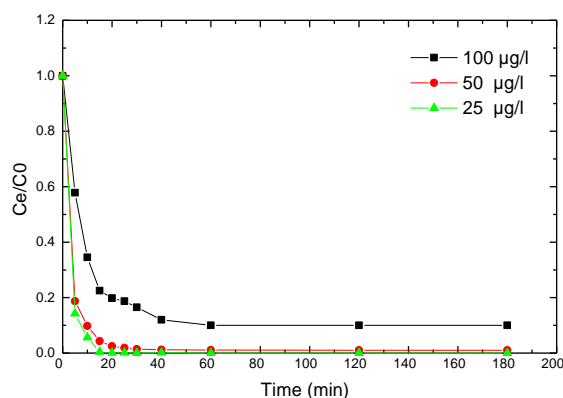
In Fig. 1, The results of the experiment of contact time showed that adsorption of p-xylene is spontaneous and very fast process. About 80-90% p-xylene was adsorbed within the first 5-25 min, then adsorption increases slowly up to saturation value was reached, the desorption equilibrium could be reached in about 30min.

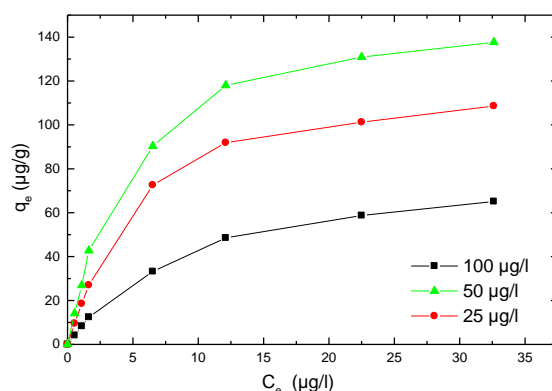
Figure 2 shows the effect of concentration (25 to 100 g/L) on the adsorption of p-xylene by FeAl/B. The data by solid line in the plot concerning p-xylene adsorption onto FeAl/B shows the fitting result using the Langmuir adsorption equation. The isotherms followed the typical Type-I behavior, suggesting a high affinity between the p-xylene and the adsorbent. It confirmed that the adsorption is monolayer coverage with homogeneous site. The saturation level of the isotherm is reached

at the low equilibrium concentration of approximately 50 µg/L and the high adsorption capacity of 274 µg/g, indicating a high degree of irreversibility of the adsorption system. The large amount adsorbed of p-xylene was due to the high surface area and micro-porous volume of FeAl/B.

**Table 3** Langmuir adsorption isotherm constants

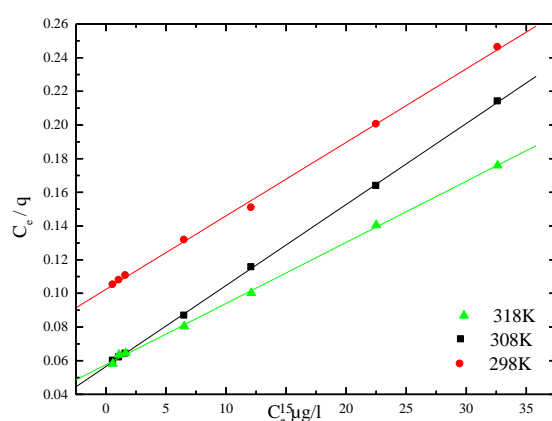
	Temperature (K)	q <sub>m</sub> (µg/g)	b (L/g)	R <sup>2</sup>
P-xylene	289	198.71	0.0369	0.999
	303	228.73	0.0631	0.999
	318	275.43	0.084	0.999

**Figure 1.** Adsorption Kinetics of p-xylene by FeAl/B



**Figure 2.** Adsorption equilibrium isotherm of p-xylene on FeAl/B at 298 K.

Fig. 3 shows the effect of temperature on adsorption capacity was investigated by measuring the adsorption isotherms at various temperatures, namely, 298, 303, and 318 K. It was observed well the data were fitted to Langmuir isotherm model. Langmuir adsorption constants and correlation coefficients (R) are also shown in Table 3. As can be seen with the increased of temperature from 298 to 318 K,  $q_m$  (µg/g) and  $b$  (L/g) values calculated with the Langmuir equation increased from 198 to 275 (µg/g) and from 0.036 to 0.084 (L/g), respectively. This observation reveals that the capacities of the aromatic compound adsorption are significantly dependent on the temperature and the nature of polycation pillaring (Fe/ Al). The large amount adsorbed of p-xylene is due to the high surface area and micro-porous volume of FeAl/B (Table 2). So, the increase of temperature favors this adsorption to occur more easily given that the activation energy can be surmounted more readily. The regression coefficients of 0.999 (Table 3) were extremely high, which indicates a good compliance with the Langmuire model indicating the adsorption of p-xylene on the FeAl/B surface as a monolayer coverage.



**Figure 3.** Linear plots of Langmuir isotherm model for removal of p-xylene by FeAl/B

#### 4. Conclusion

After, successful pillaring of bentonite clay from Maghnia, Algeria with Al/Fe polymeric was performed by 18,02 Å basal spacing and 224.3 m<sup>2</sup>/g surface area, the samples FeAl/B were chosen as adsorbent for adsorption of p-xylene. The adsorption kinetic studies show that the removal of p-xylene on Fe Al B was a rapid process, indicating cationic p-xylene has a very strong affinity on the FeAl/B surface. It was found that fit of experimental data with the linearized form of the Langmuir isotherm model with high correlation coefficient ( $R^2 > 0.99$ ). The FeAl/B has very high p-xylene adsorption capacity 275 µg/g at 318 K with 99.79%. It may be concluded that pillared bentonite may be used as a low-cost, natural and abundant source for wastewater treatment.

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