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Elaboration of Inorganic Polymer for Removal of Organic Compound by Dynamic Column Test

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Abstract

The present research aims to synthesize inorganic polymer by geopolymerization reaction and to evaluate its ability to removal organic matter from water. The inorganic polymer was prepared by activation of metakaolin by a mixture of sodium hydroxide and sodium silicate. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were employed to characterize the geo-adsorbent. The XRD and SEM analysis indicates that the formation of new phase and aluminosilicate gel after the geopolymerization process. The adsorption of cationic dye into elaborated inorganic polymer matrix was investigated by a dynamic column test. To predict the breakthrough curves and determine the main fixed bed column parameters, three kinetic models; Tomas, Bohart-Adams and Yoon-Nelson models are applied to fit the experimental data. The kinetic models of the adsorption in dynamic column confirmed that the prepared adsorbent can be used repeatedly for decolouration of water contaminated by textile dye.

Keywords: *Metakaolin; Inorganic Polymer; Organic Dye; Mobility; Column Test.*

1.Introduction

The development and growth that the industrial sector has experienced in recent years has caused toxic effluents that are difficult to manage, and among the major polluting industries are industries using synthetic dyes, such as textiles, which occupy a sufficiently important place in pollution, to be taken into account. Water pollution from organic matter is a source of environmental degradation and is of particular interest at the international level. The importance attached to the protection of the natural environment and to the improvement of the quality of the water, does not cease growing. Synthetic dyes are a source of water pollution, in fact discharges of water heavily loaded with dyes in the ecosystem generate problems of aesthetic pollution, knowing that they are clearly apparent for concentrations below 1 mg/L. They are little or no biodegradable [1]. In addition, their presence in aquatic systems, even at low concentrations, reduces the penetration of light and therefore has a detrimental effect on photosynthesis [2]. Therefore, the clearance of water contaminated by these chemicals is necessary both for the protection of the environment and for a possible reuse of these unconventional waters. For this problem, a variety of techniques such as membrane filtration [3], ultrafiltration membrane [4], ozonation [5], electrocoagulation [6] and adsorption [7] have been used to treat wastewater contaminated by organic compounds. In the context of industrial water treatment, adsorption has proved to be a very effective method for the reduction of toxic materials in aqueous medium. This is due to the ease of use of this process and the low cost compared to other applications in the process of depollution especially if the adsorbent is cheap and readily available. Many categories of adsorbents has been developed to purify water polluted by contaminants dyes such as fly ash [8], magnetic adsorbent [9], silica [10] and geopolymer [11]. Among them, inorganic polymers have received growing attention due to their low-cost adsorbent and good physical and chemical properties. The term "inorganic polymer or geopolymer" refers to synthetic mineral polymers with structure three-dimensional family of aluminosilicates [12]. This expression was introduced for the first time in 1979 by Joseph Davidovits [13]. This solid is a class of semi-crystalline aluminosilicate materials, generally synthesized at room temperature or slightly elevated by a chemical reaction between amorphous aluminosilicate powder and a highly concentrated alkaline solution [14]. In this study, metakaolin based inorganic polymer was synthesized, structurally characterized and tested by column method for the decolorization of aquatic environment contaminated by toxic textile dye.

2. Materials and methods

2.1. Materials, chemicals and instruments

Methylene Blue dye (MB) with the molecular formula $C_{16}H_{18}ClN_3S$ and molecular weight 319,852 g/mol, purchased from Sigma Aldrich. The concentrations of MB were measured at maximum absorbance (λ_{max}= 664 nm) with a spectrophotometer JASCO V-630 UV/VIS. The structural analysis was performed by X-Ray Diffraction using CuKα (Philips model 1840 equipment). The functional groups of samples were detected using Fourier transform infrared spectrometry bruker platinum ATR apparatus in the region of 4000–400 cm^{-1} wavenumbers. The microstructure was evaluated by JEOL-6300F field-scanning electron microscope (SEM/EDX). The clay was collected in the region of Ribat el kheir located 60 km from the city of Sefrou in Morocco. This material was treated at 800 °C for 3 h to obtain metakaolin. The chemical composition (wt.%) of clay measured by X-ray Fluorescence (XRF) was (SiO_2 (41.6%), Al_2O_3 (24.3), CaO (2.8%), MgO (10.1%), Fe_2O_3 (3.17%), SO_3 (3.69%), K_2O (2.02%), Na_2O (1.22%) and LOI (‘‘loss on ignition” 9.77%)).

2.2. Adsorbent synthesis

The precursor solution for activation of metakaolin was made by dissolving sodium hydroxide (NaOH, ACS AR Analytical Reagent Grade Pellets) (12M) with sodium silicate (Honeywell Riedel-de Haën, Germany; 18 wt.% Na_2O, 63 wt.% SiO_2, 18wt.% loss on ignition) at ratio $Na_2SiO_3/NaOH$=2.5 and mechanically mixing for 15 min [15]. Inorganic polymer was formulated at room temperature by mixing metakaolin with precursor solution at the mass ratio of 2.5 for 15 min. The sample was dried at 70°C for 24 h. Then the prepared solid was ground and sieved to obtain the particle size for adsorption process.

2.3. Column test

The column operation was used to evaluate the mobility and adsorption of cationic dye on the synthesized adsorbent by column of different length. Fixed bed column experiments were carried out using a glass column (diam, 1.2 cm; length, 30 cm) for adsorption of MB onto inorganic polymer at various bed height (Z=1cm (2.28 g); 3 cm (5.82 g); 5 cm (8.04 g)) by fixing influent concentration (40 mg/L) and flow rate (6 mL/min).

3. Results and discussion

3.1. Characterization of the adsorbent

3.1.1. X-ray diffraction studies

The XRD patterns of kaolin, metakaolin and inorganic polymer are presented in Fig.1. Quartz and kaolinite are the major crystalline phase of kaolin. After calcination of raw kaolin, the quartz peaks are less intense and the disappearance of kaolinite peaks can be explained by the transformation of kaolinite phase by the evaporation of water occurring in the kaolin structure (dehydroxylation reaction) [16]. After geopolymerization, the kaolinite and quartz peaks are less intense and a non-crystalline structure is formed between 20° and 26°. This result indicted a change in the chemical structure of metakaolin after geopolymerization.

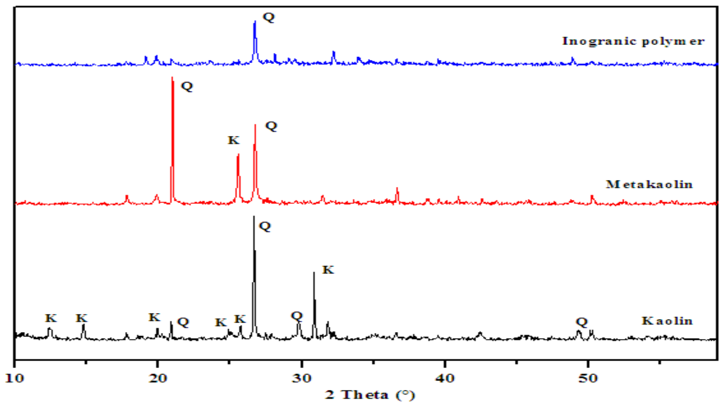

Figure 1. XRD pattern of kaolin, metakaolin and inorganic polymer (Q: Quartz; K: Kaolinite)

3.1.2. Microstructure observation

Fig. 2 shows SEM microstructures of metakaolin before (Fig.2.a) and after activation (Fig.2.b) by alkaline solution. Different sizes and heterogeneous surface are visible in the microstructure of metakaolin. After the treatment process, it can be observed that the prepared material was characterized by the formation of gel on surface of the metakaolin by dissolution of alkali activator on the surface of clay.

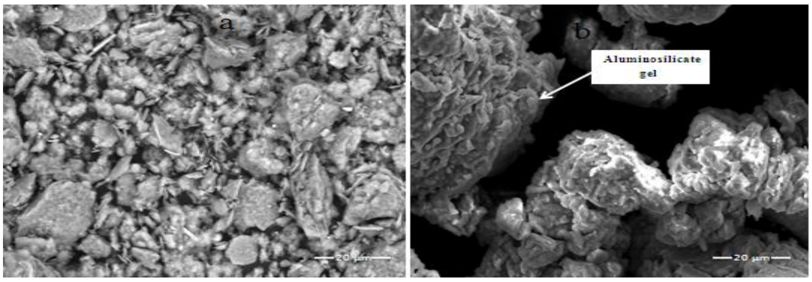

Figure 2. SEM images of (a) metakaolin and (b) inorganic polymer

3.2. Column adsorption test

The influence of bed height of the column (H = 1, 3 and 5 cm) on the mobility of MB in column containing inorganic polymer was studied at a constant initial concentration of MB solution (40 mg/L), a constant flow rate (6 mL/min) and a constant temperature (25°C) (Fig.3). The breakthrough time increased from 280 to 650 min with increasing bed height from 1 to 5 cm. This reveals that higher bed height was favorable for the removal of MB by inorganic polymer. This can be explained with the interaction between adsorbate and adsorbent which increases of the adsorption actives sites number. Several interesting study were made for the treatment of this toxic substance onto various adsorbent materials were also reported in the literature [17–19].

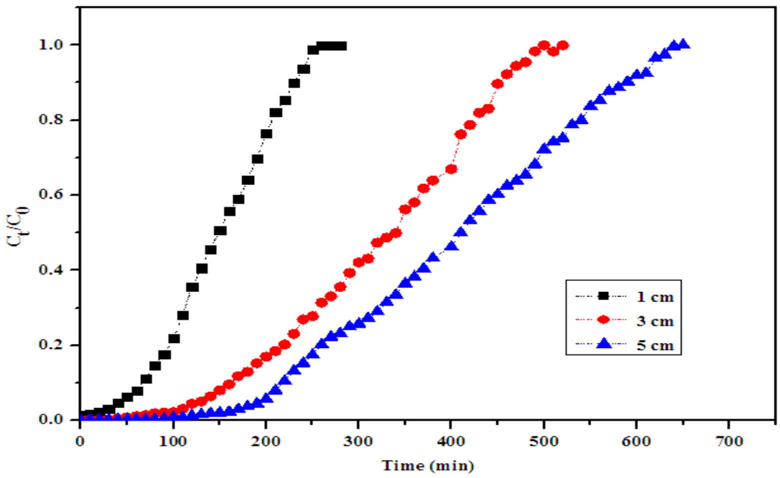

Figure 3. Breakthrough curve of the effect of different bed heights on MB adsorption on inorganic polymer

3.3. Breakthrough curves modeling

Various mathematical equations were used to describe the MB removal dynamic in the fixed bed column. The adsorption kinetics data of MB using inorganic polymer were analyzed with Thomas [20], Adams-Bohart [21] and Yoon-Nelson equations [22].

The Thomas model

The Thomas model is used to describe the adsorption kinetics in fixed bed column. The mathematical form of Thomas model is obtained by Eq (1):

$$Ln(\frac{C_0}{C}-1) = k_{th} q_0 \frac{m}{F} - k_{th} C_0 t \quad (1)$$

Where C_0 is the initial concentration (mg/L), C is the effluent concentration at the time t (mg/L), m is the mass of the adsorbent (g), F is the flow rate (mL/min), k_{th} is the Thomas model rate constant (mL/min.g) and q_0 is the maximum adsorption capacity at equilibrium (mg/g).

The Adams-Bohart model

The Adams-Bohart equation is used to describe the initial part of the breakthrough curve. The linearized form of the Adams-Bohart model can be expressed as follows Eq (2):

$$Ln\frac{C}{C_0} = k_{AB} C_0 t - k_{AB} N_0 \frac{H}{v} \qquad (2)$$

Where C_0 is the initial concentration (mg/L), C is the effluent concentration at the time t (mg/L). k_{AB} is the Adams-Bohart rate constant (min^{-1}), H is the bed depth (cm), N_0 is the volumetric sorption capacity (mg/L) and v is the linear velocity (cm/min).

The Yoon-Nelson model

The Yoon–Nelson model was applied to experimental data for the description of the breakthrough behavior of adsorbate on adsorbent. The model provides information about the break through rate in a fixed-bed column and the time entailed to achieve 50% break through [23]. The Yoon-Nelson model can be presented by Eq (3):

$$Ln\frac{C}{C_0 - C} = k_{YN} t - k_{YN} t_{50} \qquad (3)$$

Where C_0 is the initial concentration (mg/L), C is the effluent concentration at the time t (mg/L), k_{YN} is the rate constant (min^{-1}) and t_{50} is the time required for 50 % adsorbate breakthrough (min). The model parameters for mobilization of methylene blue by synthesized adsorbent are listed in Table 1. For Thomas parameter model, the rate constant k_{Th} decreased simultaneously with bed height increasing. This result can be explained by the time required to exhaust the active adsorption sites available in the adsorbent dose in a different bed height [24]. For the Yoon-Nelson mathematical model, the kinetic parameters values for rate constant k_{YN} and the time required for 50 % breakthrough at all bed height show significant difference. It can be observed that the values of k_{Th} decrease, while the values of time required for 50 % breakthrough increased with increasing the bed depth. The results obtained were in a good agreement with the experimental results of other researchers [25,26]. For the Adams-Bohart equation, it can be observed that the concentration at saturation (N_0) decreases and the kinetic constant k_{AB} decreases of adsorption of dye onto adsorbent with increasing ratio dose in column. This result can be explained by that the increase in bed height the column operation increasing availability of organic contaminant to adsorbed on the actives sites of adsorbent surface [11]. The regression coefficient R^2 for these models are ringing between 0.859-0.961, demonstrates that the three models can be successfully applied for characterization of remediation of cationic dye from aqueous solution on column tests. These results indicate that the synthesized material is considered to have good capacity for immobilization of hazardous dye contaminated water by dynamic test.

Table 1. Kinetic parameters for adsorption of MB onto inorganic polymer in the column study

Models	Thomas model			Adams-Bohart model			Yoon-Nelson model		
Bed height	**q_0 (mg/g)**	**k_{TH}**	**R^2**	**k_{AB}**	**N_0**	**R^2**	**K_{YN}**	**t_{50}**	**R^2**
1 cm	18.912	$8.75.10^{-4}$	0.858	$3.75.10^{-4}$	9208	0.887	0.035	138.11	0.858
3 cm	14.553	$4.75.10^{-4}$	0.918	$2.75.10^{-4}$	5341.09	0.849	0.019	307.52	0.918
5 cm	12.135	$3.75.10^{-4}$	0.961	$2.5.10^{-4}$	3855.80	0.862	0.015	414.93	0.961

3.4. Analysis FI-TR before and after adsorption of MB

The Fourier transform infrared spectra for inorganic polymer before and after adsorption are shown in Fig.4. For inorganic polymer, a band around 1111 cm^{-1} characteristic of the assigned bending vibration of Si-O-Si. The band at 979 cm^{-1} may indicate the Si-O-Si/Si-O-Al stretching vibration. The band appeared in the region of 664, 553 and 446 cm^{-1} were assigned to bending vibrations Si-O-Al, stretching vibrations Si-O-Al and Si-O-Si bending vibrations, respectively [27]. After the adsorption of organic dye by prepared adsorbent, the bands at 3356 and 1635 cm^{-1} are ascribed to OH stretching of water. The new bands at the region of 1396 and 1338 cm^{-1} were characteristic infrared absorption peaks of dye, which attributed to $-CH_3$ asymmetric bending vibration, C-S-C vibration [28]. These bands indicate the adsorption of molecules dye onto inorganic polymer.

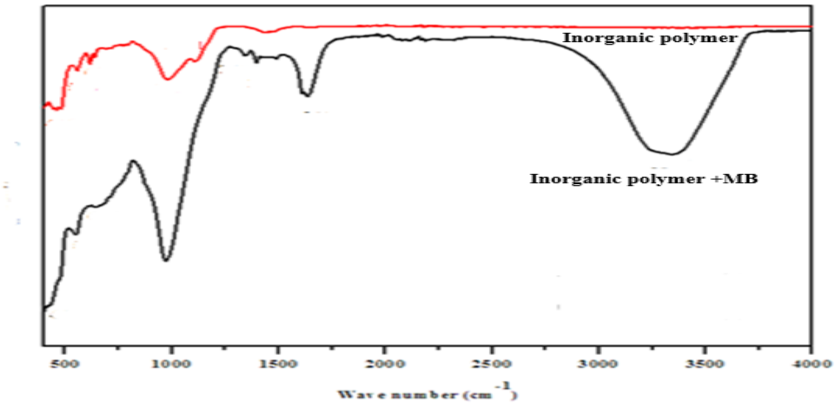

Figure 4. The FTIR spectra of inorganic polymer before and after adsorption of MB

4. Conclusion

In this work, activated kaolin was prepared in order to enhance its adsorption property of MB dye in aqueous solution by fixed-bed column. The results of the analysis by XRD and SEM show that the formation of new adsorbent by geopolymerization reaction. FTIR analysis confirms the adsorption of MB on the surface of the elaborated adsorbent. The kinetic models of the adsorption in column are suitable to describe the continuous adsorption process of textile dye by inorganic polymer.

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