EnvironmentAsia
The international journal by the Thai Society of Higher Education Institutes on Environment

EnvironmentAsia 12(1) (2019) 143-153
DOI 10.14456/ea.2019.16
ISSN 1906-1714; ONLINE ISSN: 2586-8861

Comparative Studies on Removal of Textile Dye onto Geopolymeric Adsorbents

Marouane EL Alouani*, Saliha Alehyen, Mohammed EL Achouri and M'hamed Taibi

Mohammed V University in Rabat, Laboratoire de Physico-Chimie des Matériaux Inorganiques et Organiques (LPCMIO). Ecole Normale Supérieure (ENS). Centre des Sciences des Matériaux (CSM), Morocco

* Corresponding author : ma.elalouani@gmail.com
Received: June 15, 2018; Accepted: October 14, 2018

Abstract

In the present work we performed a comparative study on the removal of organic dye by fly ash based geopolymer (FA-G) and metakaolin based geopolymer (M-G). The mineralogical and textural analyses of samples were characterized using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). XRD and SEM confirmed the formation of new geopolymer composites by geopolymerization reaction. The FTIR analysis showed that the adsorbents with good MB adsorption performance can be prepared from rich aluminosilicate materials. The effect of contact time, initial dye concentration, pH of solution and temperature were evaluated by batch test for purification of aqueous solution contaminated by dyestuff. The kinetic adsorption data were analyzed by pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The experimental data were evaluated using the linear forms of the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The best condition for maximum dye removal was found at high pH. The mechanism of kinetic adsorption by two adsorbents was described by pseudo-second-order model. Adsorption isotherms revealed that the adsorption followed a Langmuir model for adsorbents and the maximum dye adsorption capacity as predicted by Langmuir isotherm was 37.04 mg/g for FA-G and 43.48 mg/g for MK-G. On the whole, the experimental results showed that the innovative adsorbents are suitable for the effective treatment of aqueous solution contaminated with organic dye.

Keywords: Fly ash; Metakaolin; Geopolymer; Adsorption; Equilibrium isotherm; Kinetics; Textile dye

1. Introduction

The dyestuffs are being used extensively throughout the modern world. The discharge of hazardous materials in the environment affects aquatic environmental and human health. Among the most used dye in the world is methylene blue. Methylene blue as a cationic dye is hazardous micropollutant to human health and the environment. It is widely used in industry as paper, leather plastic manufacture, automotive industry and textile industry, etc. The water polluted by this dye even if the very toxic and non-degradable. For these reasons, so many works focused on the removal of organic matter from wastewater (EL Alouani *et al.*, 2018; Hajjaji and Alami, 2009; Novais *et al.*, 2018). To date, a variety of technologies such as adsorp-

tion (Al-Manhel *et al*., 2018; El Alouani *et al*., 2017), advanced oxidation (Nasuha *et al*., 2016), coagulation (Shi *et al*., 2007), electrochemical treatment (Sirés and Brillas, 2012), biological treatment (Dellamatrice *et al*., 2017) and other processes, have been developed to remove organic dyes from aqueous solutions. Among these methods, adsorption is considered as one of the most effective, simple design, low cost, use of non-toxic and ease of operation.

There are several published rapports in literature on the utilization of the natural and synthetic adsorbents for remediation of pollutants from water, such as phosphoric acid based geopolymers (Khan *et al*., 2015), fly ash based geopolymer (Li *et al*., 2006), kaolin and zeolite (Rida *et al*., 2013), activated carbon (Gopinathan *et al*., 2017), organo-bentonite (Bergaoui *et al*., 2018) and chitosan/MgO composite (Haldorai and Shim, 2014).

Several methods have been utilized to develop new adsorbents with high selectivity and high adsorption capacity. Among the techniques used to modify the adsorbent surface is geopolymerization (Park and Pour-Ghaz, 2018). The geopolymerization is the reaction the activation of the aluminosilicate source by an alkaline solution (alkali + silica). Recent years, studies on geopolymer or inorganic polymer as an adsorbent for the immobilization of hazardous materials from wastewater have been reported. It was shown that the geopolymeric materials offered higher adsorption capacity (El Alouani *et al*., 2018; Khan *et al*., 2015; Li *et al*., 2006). Geopolymer or inorganic polymer is synthesized by geopolymeration process between the aluminoslilicate materials with alkaline solution in temperature < 100°C (Davidovits, 1991; Davidovits, 1994).

The present investigation addresses the synthesis and application of geopolymer adsorbents for the removal of hazardous dye in aqueous mediums. For this purpose, the morphology and structural analyses of innovative adsorbents were characterized using XRD and SEM studies. The influence of parameters such as pH of solution, contact time, MB initial concentration and temperature on the MB adsorption by geopolymeric adsorbents was evaluated. The adsorption isotherms and kinetic models were performed to describe the mechanism of adsorption.

2. Materials and methods

2.1. Materials and chemicals

The fly ash is formed by combustion of solid biomass and obtained from Jorf Lasfar power plant in EL jaddida, Morocco. The kaolin (obtained from Sefrou in Morocco) was calcined at 800°C for 3h to procedure metakaolin. Pollutant dye: As cationic dye, basic blue 9 (Molecular formula = $C_{16}H_{18}ClN_3S$, molecular weight = 319,852 g/mol, was solubility in water =100 mg/L) was purchased from Sigma Aldrich, Germany.

2.2. Adsorbents synthesis

The adsorbents studied in this work were prepared as described by a previously published paper (Alehyen *et al*., 2017). The geopolymeric adsorbents were obtained through geopolymerization reaction. This process was divided onto two steps. The first step was the formulation the alkali solution by mixture of sodium silicate and 12 M NaOH at ratio 2.5. The second step, the fly ash based geopolymer (FA-G) and metakaolin based geopolymer (MK-G) were synthesized by mixing the samples (fly ash or metakaolin) with an alkali activator solution at ratio 2.5. The obtained products were dried at 105°C and sieved to particles size less than 200 μm for adsorption tests.

2.3. Adsorbents characterization

X-ray diffraction (XRD) patterns of samples were recorded with a high resolution powder X-ray diffractometer model Xpert Pro with Cu-Kα radiation as the X-ray source (1.54060 Å). Fourier-transform infrared spectroscopy (FTIR) measurements of the prepared adsorbents before and after MB adsorption, were recorded on a VERTEX 70 FTIR spectrometer over the range of 400–4000 cm^{-1}. Scanning electron microscopy (SEM) was used to examine surface morphology of adsorbents before and after the geopolymerization process. The concentration of MB in solution was determined

for absorbance at wavelength of 664 nm using a UV-visible spectrophotometer (JASCO V-630 UV/VIS). pH-meter model (M 210) was used for pH measurement.

2.4. Adsorption test

Batch experiments were used to determine the effects of the initial pH (2-12), initial dye concentration (10-60 mg/L) contact time (30-220 min), temperature (20-70 °C) and dosage adsorbent (m=0.1g) on the MB % removal (Eq. (1)). The pH of solution was adjusted by either 0.1 M NaOH or 0.1M HCl solutions. After each adsorption experiment, the dye solution was separated for adsorbent by centrifugation. The MB concentration in the liquid was evaluated by determining the absorbance in a spectrophotometer.

$$\%\ Removal = \frac{(C_i - C_t)}{C_i} \times 100 \quad \text{Eq.1}$$

Where Ci (mg L^{-1}) is the initial concentration and Ct (mg L^{-1}) is the concentration at time t (min). Adsorption amounts at time t, qt (mg g^{-1}), and at equilibrium, q_e (mg g^{-1}), were calculated using Eqs. (2) and (3):

$$qt = \frac{(Ci - Ct)}{m} V \quad \text{Eq.2}$$

$$qe = \frac{(Ci - Ce)}{m} V \quad \text{Eq.3}$$

Where Ce (mg L^{-1}) is the concentration at equilibrium, V (L) is the volume of the studied solution and m (g) is the mass of the adsorbent.

3. Results and discussion

3.1. Characterization of the adsorbents

3.1.1. X-ray diffraction studies

XRD patterns of kaolin, metakaolin and MK-G are shown in Fig. 1. The XRD patterns of kaolin and metakaolin are an indication that the major crystalline phases are kaolinite and quartz. The XRD pattern of the MK-G contains a no crystalline phases in region 20° to 26°, indicating a change in the chemical structure after geopolymerization reaction (Li *et al*., 2018).The XRD patterns for fly ash and FA-G are presented in Fig. 2. The results of XRD analysis of the FA and FA-G indicated that quartz and mullite were the major crystalline phase. The reduction of peak in region 22° and 28° indicated that the presence of amorphous phase. The results showed that the structure of the FA-G was a semi-crystalline material.

3.1.2. Fourier Transform Infrared Spectroscopy (FTIR) analysis

Fig. 3 shows the FTIR spectra of the FA-G sample before and after dye adsorption. The adsorption band at 1635 cm^{-1} is assigned to the bending vibration of the –OH groups. The most intensive band located at 1015 cm^{-1} due to the asymmetric Si-O-Si/Si-O-Al stretching. The bonds at 723, 542 and 426 cm^{-1} correspond to Si-O-Al bending, Si-O-Al stretching and Si-O-Si bending (Naghsh and Shams, 2017), respectively. After the retention of dye by the adsorbent, the peaks at 3453 and 1687 cm^{-1} are ascribed to OH stretching of water. The bands at 1454, 995 and 853 cm^{-1} were characteristic infrared absorption peaks of dye, which attributed to -CH3 asymmetric bending vibration and C-S-C vibration (Ovchinnikov *et al*., 2016). These bands confirm the adsorption of the methylene blue on FA-G. The infrared spectra of MK-G before and after adsorption are illustrated in Fig 4. The bands between 1100 cm^{-1} and 400 cm^{-1} correspond to the asymmetric stretching vibrations of Si–O–T (T= Si or Al). After adsorption process (Barbosa *et al*., 2018). The new bands were observed at 1338, 1396 and 1635 cm-1and indicate the presence of –C=N-, C-N-C and C=C stretching in polyheterocycles (Sakin Omer *et al*., 2017). The peak at 3356 cm^{-1} corresponds to the presence of OH stretching of hydroxyl group. On the basis of this result one can confirm the adsorption of cationic dye on adsorbent surface.

3.1.3. Microstructure observation

Fig. 5 (a) and (b) shows the SEM micrographs of the metakaolin and MK-G. The surface morphology of the metakaolin was different from that of the MK-G. SEM images (Fig.5.a) of metakaolin has a heterogeneous material consisting of irregularly shaped particles.

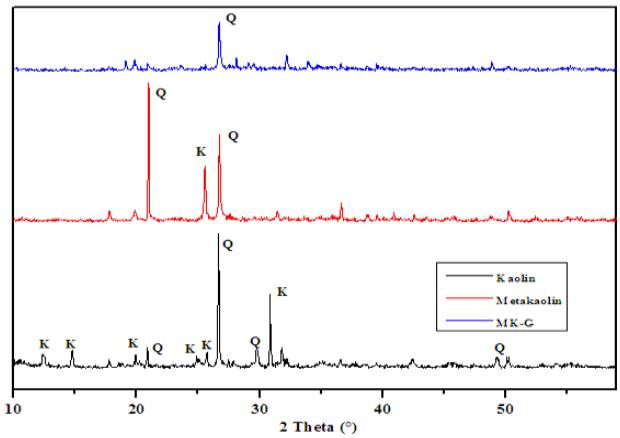

Figure 1. XRD patterns of kaolin, metakaolin and MK-G (Q: Quartz, K: Kaolinite)

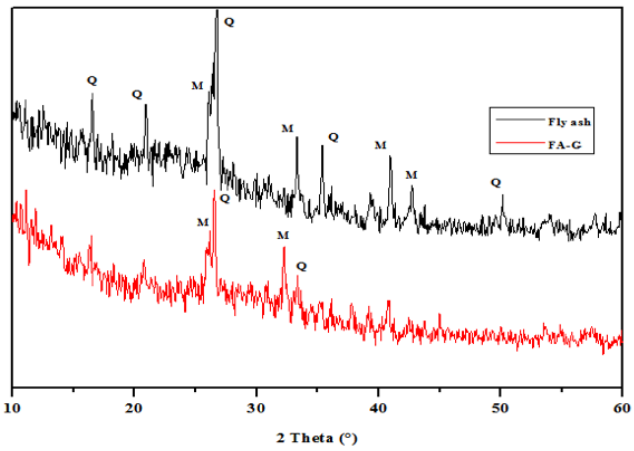

Figure 2. XRD patterns of fly ash and FA-G (Q: Quartz, M: Mullite)

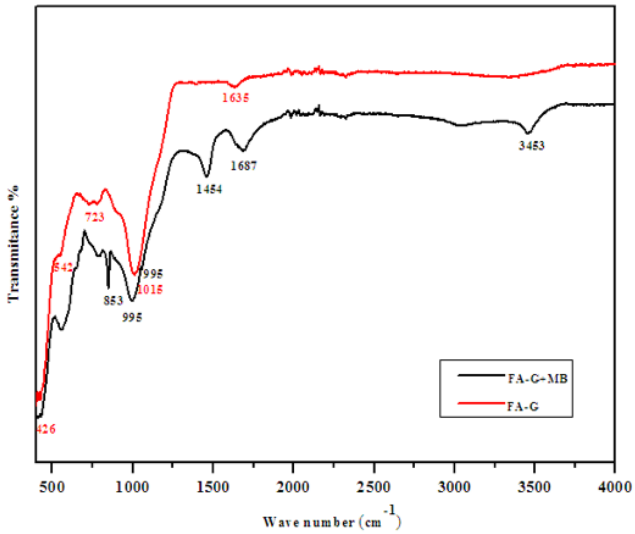

Figure 3. The FTIR spectra of FA-G before and after the adsorption of dye

After geopolymerization reaction, the microstructure of MK-G which has porous and homogenous surface after activation reaction. This result indicates that the formation of amorphous solid after activation process by gel formed on the surface of the metakaolin particle.

The changes in the morphology of fly ash and FA-G are reported in Fig. 6 (a) and (b).The fly ash is composed of spherical particles of different sizes (microspheres) and this material is characterized by a crystalline phases (Quartz and Mullite) (Fig.6(a)). After activation process (Fig. 6(b)), the microstructures of developed material show that the microspheres of the fly ash were dissolved by aluminosilicate gel. This result reveals that the crystalline structure disappeared and transformed to an amorphous state.these observations indicate that the surfaces of prepared adsorbents have selective and high capability for the adsorption of dyes from aqueous mediums.

3.2. Batch operation

3.2.1. Effect of pH

The pH of a solution is the most influential parameter for removal of pollutant from wastewater. The effect of solution pH on the adsorption of MB onto FA-G and MK-G was investigated and results are presented in Fig. 7. It was observed that the adsorption of MB on the two adsorbents increased as the pH of the solution increased from 2 to 12. It was also noted that the adsorption of MB was favored at high pH. This result can be explained by the competition between H^+ and MB^+ ions for activated adsorption sites on the geopolymeric adsorbents surface at acidic pH. With the increase in pH, less H^+ is available leading to better access of MB toward the active sites (Tumin *et al.*, 2008).

3.2.2. Effect of contact time

The influence of contact time of geopolymeric adsorbents on the adsorption of MB in range of 0-220 min is undertaken to determine the optimal demanded time for removing 40 mg/L of dye solution at pH = 5 and T=25°C. The effect of contact time on the adsorption of MB by FA-G and MK-G is illustrated in Fig. 8. As we can observe from Fig.8, the removal of dye increases significantly in the first 30 minutes and was reached in about 150 minutes. For the FA-G, the removal of dye increased with increment of contact time, reaching equilibrium after 150 min and attaining at approximately 98.5% of removal. For the MK-G, the removal of MB increased from 87.50 to 97.90 % when contact time was increased from 30 to 150 min. Indeed,

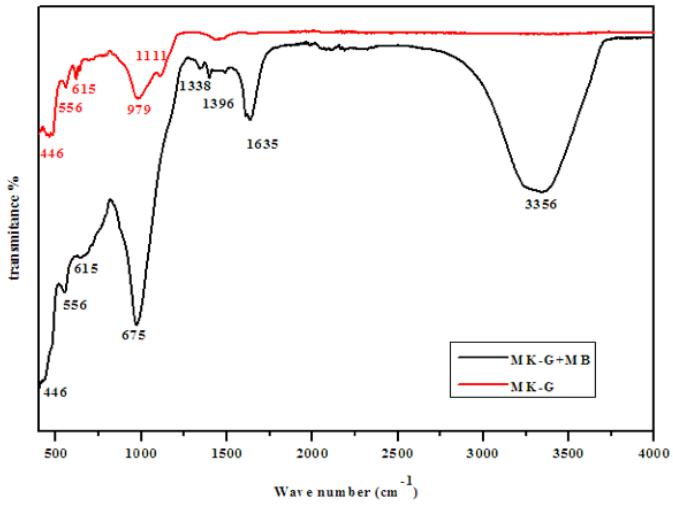

Figure 4. The FTIR spectra of MK-G before and after the adsorption of dye

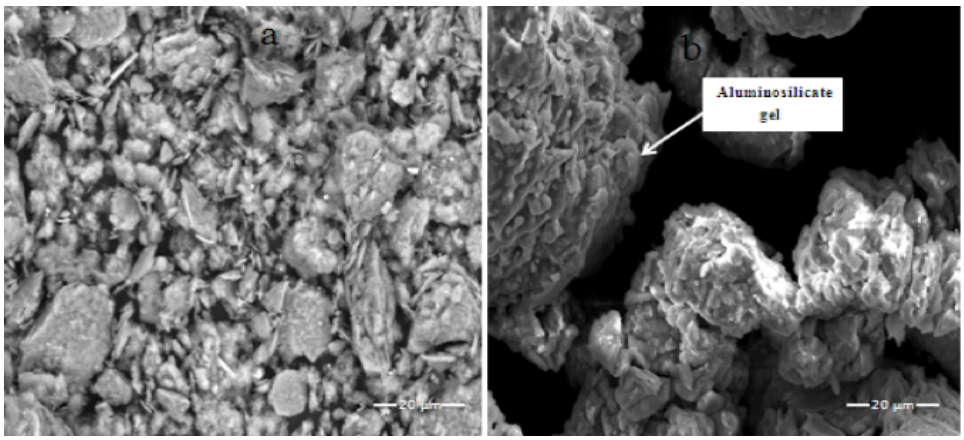

Figure 5. SEM micrographs of metakaolin (a) and MK-G (b)

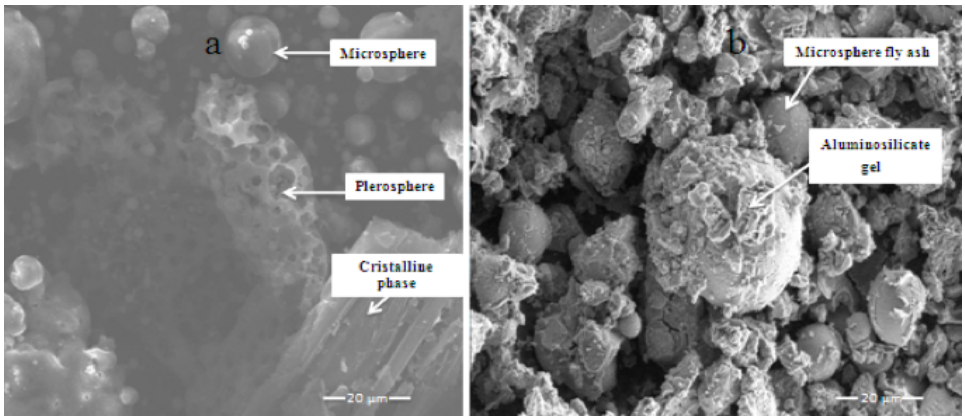

Figure 6. SEM micrographs of fly ash (a) and FA-G (b)

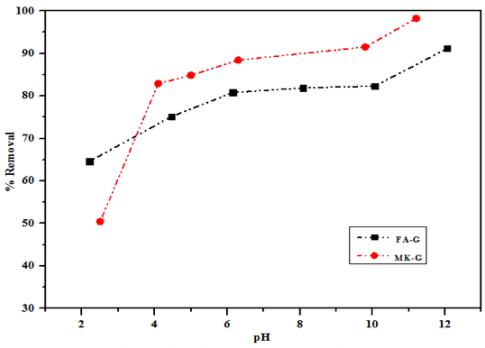

Figure 7. Effect of solution pH on the adsorptions of MB by MK-G and FA-G (initial MB dye concentration = 40 mg/L, time = 120 min, adsorbent dose = 0.1g, temperature = 25°C)

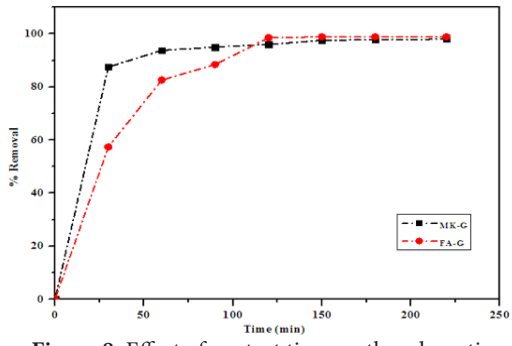

Figure 8. Effect of contact time on the adsorptions of MB on MK-G and FA-G (initial MB dye concentration = 40 mg/L, adsorbent dose = 0.1g, pH = 5, temperature= 25°C)

this can be explained by the adsorbents reaching saturation in approximately 150 minutes.

3.2.3. Effect of initial concentration of MB

The adsorption of MB by geopolymeric adsorbents was studied at different initial concentration (5-10-30-40-60 mg/L). The effect of initial concentration of cationic dye is show in Fig. 9. The adsorption capacity of MB onto synthesized materials changes from 4.89 to 36.44 mg/g of FA-G and 4.95 to 41.14 mg/g of MK-G. This augmentation can be explained by the high driving of mass transfer of dye from solution to the surface structure of solid adsorbents (Kara *et al.*, 2018).

3.2.4. Adsorption kinetics study

Various kinetic models, including pseudo-first-order model (Lagergren, 1898), pseudo-second-order (Ho and McKay, 1999) and intra-particule diffusion model (Shakoor and Nasar, 2016) have been utilized to explore the mechanism of adsorption MB onto adsorbents. The obtained kinetic parameters are presented in Table 1. The correlation coefficients for the pseudo-second-order kinetic model (R^2=0.990 for FA-G and 0.999 for MK-G) were higher than for the pseudo-first-order kinetic model (R^2=0.926 for FA-G 0.936 for MK-G) and intra-particule diffusion model (R^2=0.796 for FA-G and 0.692 for MK-G) and the theoretical qe,cal values were closer to the experimental qe,exp values. These results demonstrated that the adsorption of MB onto geopolymeric adsorbents follows the pseudo second order kinetic model and the adsorption is controlled by the chemisorption process (Mouni *et al.*, 2018).

3.2.5. Adsorption isotherms study

The Freundlich (Freundlich and Heller, 1939), Langmuir (Wong *et al.*, 2003), Temkin (Peng *et al.*, 2014) and Redlich–Peterson (Redlich and Peterson, 1959) isotherm models were used to describe the isotherms of MB adsorption onto FA-G and MK-G. The fitting of experimental isotherms data is illustrated in Table 2. The isotherm data showed a better fit to the Langmuir isotherm model with the R^2 values of 0.994 for MK-G and 0.999 for FA-G. Based on the Langmuir isotherm model, the maximum monolayer adsorption capacity for MB using FA-G was 37.04 mg·g^{-1} and 43.84 mg·g^{-1} onto MK-G. In addition, the values of RL were between 0 and 1 indicating that the adsorption of MB onto MK-G and FA-G was favorable.

3.2.6. Effect of temperature

The effect of temperature is one of the most important factors to describe the adsorption process. Fig.10 shows the effect of temperature on the adsorption of MB on elaborated adsorbents in the range of 20–70°C. The experimental results show that the amount of adsorbed dye increased with increase in the solution temperature from 20 to 70 °C, as expected for an endothermic adsorption process. This trend that the increasing the temperature increases the

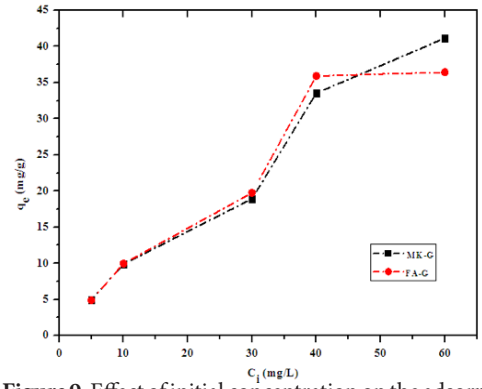

Figure 9. Effect of initial concentration on the adsorption of the dye onto MK-G and FA-G (Adsorbent dose =0.1 g, pH = 5, time = 120 min, temperature = 25°C)

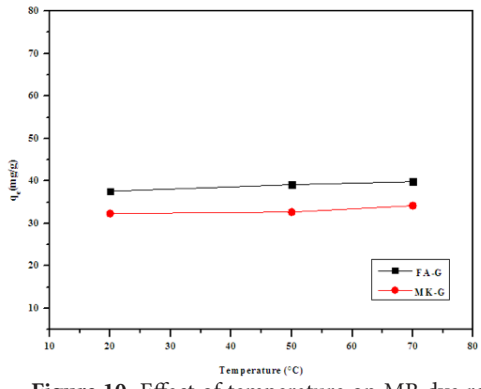

Figure 10. Effect of temperature on MB dye removal (initial MB dye concentration = 40 mg/L, adsorbent dose=0.1 g, pH = 5, time= 120 min)

Table 1. The kinetic parameters for MB adsorption on MK-G and FA-G

		Pseudo-first-order $\ln(q_e - q_t) = \ln q_e - k_1 t$				**Pseudo-second-order** $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$			**Intra-particule diffusion model** $q_t = k_1 t^{1/2}$		
Adsorbents	C_0(MB) mg/L	q_{exp} (mg/g)	q_e (mg/g)	k^1 (1/min)	$R1^2$	q_e (mg/g)	k^2 (g/mg min)	$R2^2$	I (mg/g)	kid (mg/g min0.5)	$R3^2$
FA-G	40	39.55	87	0.051	0.926	43.47	0.002	0.99	17.84	1.678	0.796
MK-G	40	39.2	18.17	0.029	0.936	40	0.0098	0.999	11.64	2.334	0.692

Where qe (mg g^{-1}) and qt (mg g^{-1}) are the amount of MB adsorbed at equilibrium and time, respectively; k^1 (1/min), k^2 (g $mg^{-1}min^{-1}$) and kI (mg g^{-1} $min^{0.5}$) are first-order, second-order and weber-morris model the rate constants, respectively, and I is the intraparticle diffusion constants (mg/g).

Table 2. Isotherm parameters for MB adsorption on MK-G and FA-G

	Langmuir $\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_e}$				**Freundlich** $\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$			**Temkin** $q_e = B_T \ln A_T + B_T \ln C_e$			**Dubinin–Radushkevich** $q_e = \ln q_m + K\varepsilon^2$		
	Qm (mg/g)	KL (L/mg)	R2	Range RL	KF ($mg1^{-1/n}$/ L1/n/g)	1/n	R2	AT (L/g)	BT	R2	Qm (mg/g)	R2	E (Kj/mol)
MK-G	43.48	1.15	0.994	0.014-0.15	17.18	0.332	0.963	43.38	5.897	0.98	30.57	0.915	5.77
FA-G	37.04	3.38	0.999	0.05-0.56	18.78	0.271	0.694	105.64	5.094	0.866	28.61	0.555	5

Where qm is the maximum adsorption capacity ($mg{\cdot}g^{-1}$), RL values indicate the type of isotherm to be irreversible (RL= 0), favorable (0<RL<1), linear (RL = 1) or unfavorable (RL>1) KL is the Langmuir constant ($L{\cdot}mg^{-1}$), and KF and n are Freundlich constants, AT is the Temkin isotherm constant (L/g), BT is corresponding to the heat of adsorption and E (Kj/mol) is the energy of adsorption.

activation of adsorbents surfaces sites and the increases rate of diffusion of molecule dye insurface of adsorbents.

4. Conclusion

The present work focused on the adsorbents synthesis from aluminosilicate materials with activation by alkaline solution and its application for adsorption of methylene blue from aqueous medium by batch test. The adsorption capacity of MB on adsorbents increased with increasing the initial concentration of dye and pH values of the aqueous medium contaminated by cationic dye. The kinetic data was found to fit well to the pseudo second order kinetic model. The equilibrium adsorption data was best fitted by the Langmuir isotherm and the maximum adsorption capacity (qm) was 37.04 mg/g for FA-G and 43.48 mg/g for MK-G. Based on the present investigation, the materials synthesized in this aim is a new alternative adsorbents, presenting high adsorption capacity for remove of cationic dye in aquatic environment.

References

Alehyen S, Zerzouri M, ELalouani M, EL Achouri M, Taibi M. Porosity and fire resistance of fly ash based geopolymer. Journal of Materials and Environmental Science 2017; 8 (10): 3676-3689.

Al-Manhel AJ. Al-Hilphy ARS. Niamah AK. Extraction of chitosan, characterisation and its use for water purification. Saudi Society of Agricultural Sciences 2018; 17: 186–190.

Barbosa TR, Foletto EL, Dotto GL, Jahn SL. Preparation of mesoporous geopolymer using metakaolin and rice husk ash as synthesis precursors and its use as potential adsorbent to remove organic dye from aqueous solutions. Ceramics International 2018; 44: 416–423.

Bergaoui M, Nakhli A, Benguerba Y, Khalfaoui M, Erto A, Soetaredjo FE, Ismadji S, Ernst B. Novel insights into the adsorption mechanism of methylene blue onto organo-bentonite: Adsorption isotherms modeling and molecular simulation. Journal of Molecular Liquids 2018; 272: 697–707.

Davidovits J. Properties of geopolymer cements. First Int. Conf. Alkaline Cem. Concr. 1994; 131–149.

Davidovits J. Inorganic polymerie new materials. J. of Thamal Analysis 1991; 37: 1633–1656.

Dellamatrice PM, Silva-Stenico ME, Moraes LABd, Fiore MF, Monteiro RTR. Degradation of textile dyes by cyanobacteria. Brazilian Journal of Microbiology 2017; 48: 25–31.

El Alouani M, Alehyen S, EL Achouri M, Taibi M. Potential use of moroccan fly ash as low cost adsorbent for the removal of two anionic dyes (indigo carmine and acid orange). Journal of Materials and Environmental Science 2017; 8: 3397–3409.

EL Alouani M, Alehyen S, EL Achouri M, Taibi M. Removal of Cationic Dye – Methylene Blue - from Aque ous Solution by Adsorption on Fly Ash - based Geopolymer. Journal of Materials and Environmental Science 2018; 9: 32–46.

El Alouani M, Alehyen S, El Achouri M, Taibi M. Adsorption of cationic dye onto fly ash-based geopolymer: Batch and fixed bed column studies. MATEC Web Conf. 2018; 149,02088.

Freundlich H, Heller W. The Adsorption of cis - and trans -Azobenzene. Journal of the American Chemical Society 1939; 61: 2228–2230.

Gopinathan R, Bhowal A, Garlapati C. Thermodynamic study of some basic dyes adsorption from aqueous solutions on activated carbon and new correlations. The Journal of Chemical Thermodynamics 2017; 107: 182–188.

Hajjaji M, Alami A. Influence of operating conditions on methylene blue uptake by a smectite rich clay fraction. Applied Clay Science 2009; 44: 127–129.

Haldorai Y, Shim JJ. An efficient removal of methyl orange dye from aqueous solution by adsorption onto chitosan/MgO composite: A novel reusable adsorbent. Applied Surface Science 2014; 292: 447–453.

Ho Y, McKay G. Pseudo-second order model for

sorption processes. Process Biochemistry 1999; 34: 451–465.

Kara I, Tunc D, Sayin F, Akar S.T. Study on the performance of metakaolin based geopolymer for Mn(II) and Co(II) removal. Applied Clay Science 2018; 161: 184–193.

Khan MI, Min TK, Azizli K, Sufian S, Ullah H, Man Z. Effective removal of methylene blue from water using phosphoric acid based geopolymers: synthesis, characterizations and adsorption studies. RSC Advances 2015; 5:61410–61420.

Lagergren S. Zur theorie der sogenannten adsorption geloster stoffe. K. Sven. Vetenskapsakademiens Handl. 1898; 24: 1–39.

Li L, Wang S, Zhu Z. Geopolymeric adsorbents from fly ash for dye removal from aqueous solution. Journal of Colloid and Interface Science 2006; 300: 52–59.

Li X, Rao F, Song S, Corona-Arroyo MA, Ortiz-Lara N, Aguilar-Reyes E.A. Effects of aggregates on the mechanical properties and microstructure of geothermal metakaolin-based geopolymers. Results in Physics 2018; 11: 267–273.

Mouni L, Belkhiri L, Bollinger J-C, Bouzaza A, Assadi A, Tirri A, Dahmoune F, Madani, K, Remini H. Removal of Methylene Blue from aqueous solutions by adsorption on Kaolin: Kinetic and equilibrium studies. Applied Clay Science 2018; 153: 38–45.

Naghsh M, Shams K. Synthesis of a kaolin-based geopolymer using a novel fusion method and its application in effective water softening. Applied Clay Science 2017; 146: 238–245.

Nasuha N, Ismail S, Hameed BH. Activated electric arc furnace slag as an efficient and reusable heterogeneous Fenton-like catalyst for the degradation of Reactive Black 5. Journal of the Taiwan Institute of Chemical Engineers 2016; 67: 235–243.

Novais RM, Ascensão G, Tobaldi DM, Seabra MP, Labrincha JA. Biomass fly ash geopolymer monoliths for effective methylene blue removal from wastewaters. Journal of Cleaner Production 2018; 171: 783–794.

Ovchinnikov OV, Evtukhova AV, Kondratenko TS, Smirnov MS, Khokhlov VY, Erina OV. Manifestation of intermolecular interactions in FTIR spectra of methylene blue molecules. Vibrational Spectroscopy 2016; 86: 181–189. 6

Park S, Pour-Ghaz M. What is the role of water in the geopolymerization of metakaolin. Construction and Building Materials 2018; 182: 360–370.

Peng X, Huang D, Odoom-Wubah T, Fu D, Huang J, Qin Q. Adsorption of anionic and cationic dyes on ferromagnetic ordered mesoporous carbon from aqueous solution: Equilibrium, thermodynamic and kinetics. Journal of Colloid and Interface Science 2014; 430: 272–282.

Redlich O, Peterson DL. A Useful Adsorption Isotherm. Journal of Physical Chemistry 1959; 63: 1024–1024.

Rida K, Bouraoui S, Hadnine S. Adsorption of methylene blue from aqueous solution by kaolin and zeolite. Applied Clay Science 2013; 83–84: 99–105.

Sakin Omer O, Hussein MA, Hussein BHM, Mgaidi A. Adsorption thermodynamics of cationic dyes (methylene blue and crystal violet) to a natural clay mineral from aqueous solution between 293.15 and 323.15 K. Arabian Journal of Chemistry 2017.

Shakoor S, Nasar A. Removal of methylene blue dye from artificially contaminated water using citrus limetta peel waste as a very low cost adsorbent. Journal of the Taiwan Institute of Chemical Engineers 2016; 66: 154–163.

Shi B, Li G, Wang D, Feng C, Tang H. Removal of direct dyes by coagulation: The performance of preformed polymeric aluminum species. Journal of Hazardous Materials 2007; 143: 567–574.

Sirés I, Brillas E. Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review. Environment International 2012; 40: 212–229.

Tumin ND, Chuah AL, Zawani Z, Rashid SA. Adsorption of copper from aqueous solution by elais guineensis kernel activated carbon. Journal of Engineering Science and Technology 2008; 3: 11.

Wong YC, Szeto YS, Cheung WH, McKay G. Equilibrium Studies for Acid Dye Adsorption onto Chitosan. Langmuir 2003; 19: 7888–7894.