



ORIGINAL ARTICLE

Adsorbent materials based on a geopolymer paste for dye removal from aqueous solutions



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Abstract Geopolymers are porous materials that can be used as basic dye adsorbents in wastewater treatment. In this work, a green geopolymer paste synthesized from industrial and agricultural waste materials was employed as an adsorbent to remove the basic dye methylene blue from aqueous solutions. The geopolymer sample was characterized by X-ray fluorescence, scanning electron microscopy, Brunauer Emmet Teller surface area measurements, and particle size techniques. The isotherms of dye adsorption by the geopolymer sample were considered by the Langmuir and Freundlich adsorption models. The removal efficiency increased with increasing geopolymer dosage, contact time and temperature. The Freundlich isotherm exhibited the best fit to the adsorption data. © 2018 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Currently, many researchers are studying geopolymer materials because of their high chemical stability, good compressive strength, high durability, and high thermal stability. Geopolymers or inorganic polymers are a class of aluminosilicate materials with amorphous polymeric structures that can be employed in many applications (Memon et al., 2011). Sustain-

able development goals have spurred advances in geopolymer materials because these materials can be synthesized at relatively low manufacturing temperatures from different industrial and agricultural waste materials, enabling significant quantities of waste materials to be recycled into new products.

Many researchers have studied the use of geopolymer materials in different applications such as passive cooling systems, thermal insulation, and porous building materials (Novais et al., 2016; Okada et al., 2009, 2011; Onutai et al., 2016). Although most research has focused on the use of geopolymers in concrete applications, these materials are thought to be excellent materials for use in evaporative cooling systems (Emdadi et al., 2016). Geopolymers are currently receiving much attention because they are viable and economical materials that can replace inorganic materials in the previously mentioned applications. Importantly, geopolymer use offers

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a new effective route to achieving environmentally friendly objectives in industry. Furthermore, geopolymers show promise for use as adsorbents for dye removal from aqueous solutions (Li et al., 2006). Several factors, including the mixture combination (Bayat, 2002; van Jaarsveld et al., 2002), adsorbent dosage (Bayat, 2002; Misra et al., 2008), pH (Cetin and Pehlivan, 2007; Naseem and Tahir, 2001), temperature (Bakharev, 2006; Misra et al., 2008; Naseem and Tahir, 2001; van Jaarsveld et al., 2002), and contact time (Cetin and Pehlivan, 2007; Misra et al., 2008), affect the sorption capacity, as shown by previous research. Moreover, geopolymer paste manufacturing has potential for effectively and inexpensively managing agricultural waste materials, making it an environmentally friendly process.

Recently, materials such as fly ash (Li et al., 2006; Lopez Guzman, 2014), RHA (Sharma et al., 2010), and MK (Setthaya et al., 2017) were used to fabricate geopolymers, and their ability to adsorb methylene blue from a solution was investigated. In our previous study, geopolymer pastes synthesized from agricultural and industrial waste materials, including rice husk (RH), rice husk ash (RHA), metakaolin (MK), palm oil fuel ash (POFA), and ground granulated blast furnace slag (GGBS), were used in evaporative cooling materials (Emdadi et al., 2017). In this study, the potential of a geopolymer paste as an adsorbent for removing the basic dye methylene blue (MB) from aqueous solutions was investigated.

2. Experimental methods

2.1. Materials

All the chemical materials used in this study were purchased as analytical grade reagents. Following our previous study, the raw materials used to synthesize the geopolymer pastes, i.e., RH, RHA, POFA, and GGBS, were prepared from local and industrial waste materials from Malaysia. MK was obtained from Burgess (USA). For the sorption measurements, the concentration of methylene blue remaining in solu-

tion was determined by UV spectroscopy measurements at $\lambda = 665$ nm (Shimadzu, model 2450).

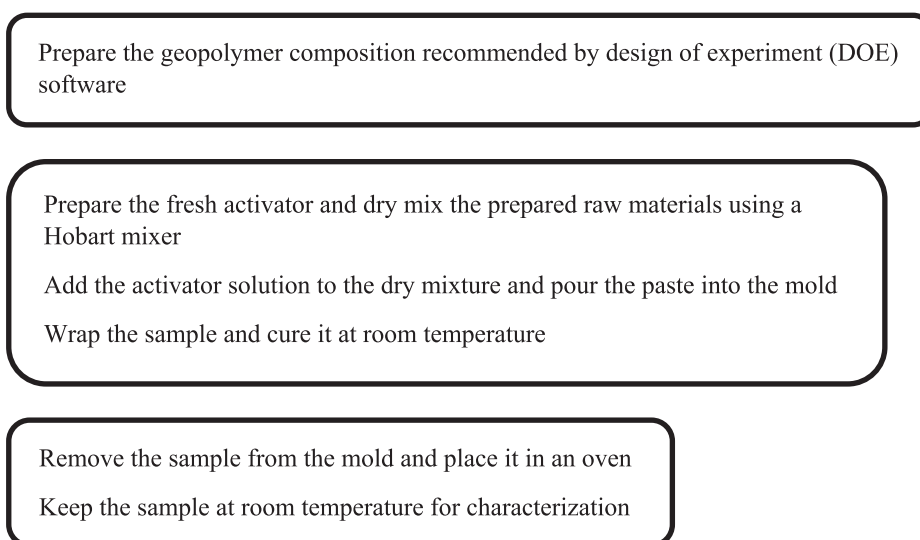
The material particle sizes were measured using a Malvern Zetasizer ZS instrument. The surface area of the sample as a texture property was determined by Brunauer Emmet Teller method (BET) using nitrogen adsorption instrument (Micrometecs ASAP 2010). The sample chemical composition (%) was determined by X-ray fluorescence (XRF) (S8 Tiger, Bruker, USA). The morphology of the prepared sample was examined by scanning electron microscopy (SEM) (Carl Zeiss-Merlin Compact, Germany).

2.2. Synthesis of geopolymer paste

The geopolymer paste samples were prepared according to the method described in Scheme 1, which was used in a previous study. As shown by our previous experimental results, one of the fabricated samples exhibited high water absorption capacity, compressive strength, porosity, and capillary rise (Emdadi et al., 2017) and was therefore used in the current study. This geopolymer sample, which was denoted SSGS, was a mixture of 10% RH, 15% RHA, 35% MK, 10% POFA, and 30% slag. The geopolymer paste samples were washed with deionized water to remove excess sodium hydroxide (NaOH) and then crushed to obtain smaller particles for the experiments.

2.3. Adsorption on the geopolymer paste

For the sorption study, the basic dye methylene blue was employed, and the experimental conditions were optimized to maximize the removal efficiency and adsorption capacity. A 10^{-4} M stock solution was prepared and used to prepare solutions with the desired concentrations for the adsorption tests. In this study, 100 ml of the dye solution was poured into a 200 ml beaker, the solid geopolymer powder was added to the beaker, and the mixture was shaken under different conditions. The removal efficiency was calculated using Eq. (1):



Scheme 1 Preparation of the geopolymer samples.

Table 1 Effective factors on sorption capacity.

Adsorption parameters	Dye concentration (M)	Adsorbents dosage (g)	Contact times (h)	Temperatures (°C)	pH value
Geopolymer dosage	10^{-5}	0.05 0.1	24	25	3
Temperature	10^{-5}	0.1	24	25 35 50	3
Contact time	10^{-5}	0.1	0.5 1 2 24	25	3
MB solution	10^{-4} 10^{-5} 10^{-6}	0.1	24	25	3
pH value	10^{-5}	0.1	24	25	3 4 5 6 7 8

$$\text{Removal efficiency (RE) (\%)} = \frac{C_0 - C_{eq}}{C_0} \times 100 \quad (1)$$

where C_0 and C_{eq} are the initial and equilibrium methylene blue concentrations (M), respectively.

The adsorption capacity was calculated using equation (2):

$$\text{Adsorption capacity (q)} = \frac{(C_0 - C_{eq}) \times V}{m} \quad (2)$$

where q is the amount of dye adsorbed by the geopolymer paste (adsorbent), V is the volume (l), and m is the geopolymer weight (g).

2.3.1. The effect of dye concentration

The effects of the dye solution concentration were investigated in the range of 10^{-6} – 10^{-5} M using a fixed geopolymer paste dosage of 0.1 g at pH 3, as shown in Table 1. The solution was stirred for 24 h at room temperature. Then, the dye concentration was measured, and the removal efficiency and adsorption capacity were calculated.

2.3.2. The effect of pH value

A mixture of the geopolymer sample (0.1 g) and a 10^{-5} M methylene blue solution (100 ml) was stirred at room temperature for 24 h at various pH values (3.0–8.0). Dilute nitric acid (HNO_3) was used to adjust the pH. The removal efficiency and adsorption capacity were measured when the system reached equilibrium.

2.3.3. The effect of adsorbent dosage

The equilibrium concentration was measured at various geopolymer dosages, and the removal efficiency and adsorption capacity were calculated. The experimental conditions were: 100 ml of a 10^{-5} M methylene blue solution, pH 3, and room temperature.

2.3.4. The effect of contact time

The effects of the contact time on the dye adsorption by the geopolymer paste samples were determined using 100 ml of a 10^{-5} M methylene blue solution and 0.1 g of the paste sample at pH 3 and room temperature. The removal efficiency and adsorption capacity were calculated at contact times ranging from 30 min to 30 h.

2.3.5. The effect of temperature

Methylene blue adsorption was studied at both room temperature (± 25 °C) and ± 50 °C to determine the effects of temperature on the adsorption capacity and removal efficiency. The other experimental parameters were 0.1 g of the geopolymer sample, 100 ml of a 10^{-5} M methylene blue solution, pH 3, and the desired contact time.

3. Results and discussion

3.1. Geopolymer characterization

Table 2 shows the physical properties of the raw materials used to prepare the geopolymer paste and the specific synthesized geopolymer sample (SSGS). As shown in the table, the particle sizes of the constituent materials and synthesized sample were fine. Because the relative densities and weights of the materials can be determined by comparing their specific gravities, the specific gravities of the materials were measured according to the standard testing protocol BS1377 (1990) (1377-2 BS, 1990).

Moreover, the chemical compositions (%) of the dry mixed samples before and after activation (denoted BSSGS and SSGS, respectively) were determined and presented in Table 3. The presence of SiO_2 and Al_2O_3 precursors was required for the synthesis of the geopolymer paste. Furthermore, the absence of toxic heavy metals was confirmed by XRF. Clearly,

Table 2 The physical properties of constituent materials of geopolymer paste and specific sample.

Materials	Physical properties
Raw RH	The specific gravity: 0.87 The BET surface area: 1.11 m ² /g Color: Brownish The particle size: 3.02 μm
RHA	The specific gravity: 2.11 The BET surface area: 16.55 m ² /g Color: Gray The particle size: 0.76 μm
POFA	The specific gravity: 2.41 The BET surface area: 3.44 m ² /g Color: Deep gray The particle size: 1.55 μm
MK	The specific gravity: 2.41 The BET surface area: 12.26 m ² /g Color: Off white The particle size: 2.35 μm
Slag	The specific gravity: 2.81 The BET surface area: 4.21 m ² /g Color: Off white The particle size: 1.50 μm
Dry mixing of materials (without activator)	The specific gravity: 1.24 The BET surface area: 13.2 m ² /g Color: Light gray The particle size: 1.3 μm
SSGS	The specific gravity: 1.1 The BET surface area: 5.80 m ² /g Color: Gray The particle size: 1.07 μm

Table 3 The percentage of chemical composition of dry mixing of raw materials and geopolymer sample by XRF (mass %).

% Chemical composition	BSSGS	SSGS
SiO ₂	54.6	52.0
Al ₂ O ₃	30.9	19.9
Fe ₂ O ₃	0.9	1.3
Na ₂ O ₃	0.2	8.5
CaO	0.9	7.6
Others	3.98	5.04
Loss on ignition	5.4	5.8
SiO ₂ /Al ₂ O ₃	1.76	2.6

the sodium content increased after geopolymerization, due to the incorporation of the NaOH hydroxyl group during geopolymer synthesis. The SiO₂/Al₂O₃ ratio increased from 1.76 to 2.6 after activation due to the alkali activator used in the geopolymerization process. The synthesized geopolymers had strongly negatively charged surfaces, which could impact the adsorption of the cationic dye considerably (Li et al., 2006). The loss on ignition (LOI), which is representative of the carbon content, was determined according to ASTM C114-04 (ASTM, 2004).

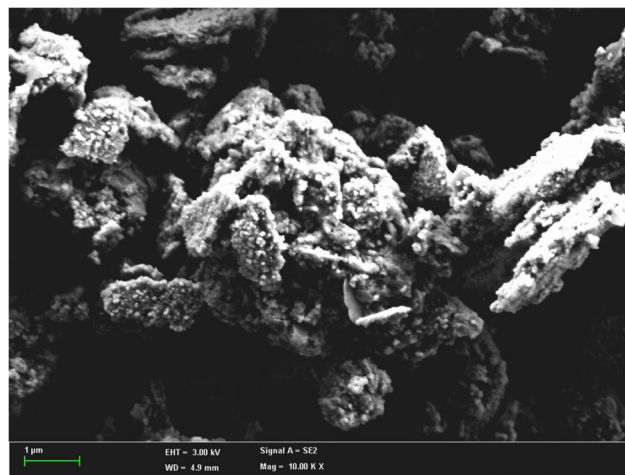
The morphology and structural features of the synthesized SSGS geopolymer sample was characterized by scanning electron microscopy (SEM). The sample consisted of uniform granules. The sponge-like gel structure observed in Fig. 1 confirmed the successful geopolymerization of the raw materials.

3.2. Dye adsorption considerations

The dye removal efficiencies of the geopolymer samples before (BSSGS, mixed dry sample) and after (SSGS) activation with alkaline activators was investigated. The following conditions were employed to determine the removal efficiencies: initial methylene blue concentration = 10⁻⁵, contact time = 24 h, adsorbent dosage = 0.1 g, and room temperature. The removal efficiencies of BSSGS and SSGS were 69.5% and 80.5%, respectively. Based on this metric, the performance of the geopolymer paste (SSGS) was higher than that of BSSGS. It was concluded that geopolymerization resulted in a distribution of pore sizes, which improved the removal efficiency and adsorption capacity (Al-Zboon et al., 2011; Wang et al., 2007). Because the synthesized geopolymer has a negative surface charge, which is due to the aluminosilicate structure (Emdadi et al., 2017; Rangan, 2008) and is affected by the pH, it can adsorb the cationic dye on its surface (Li et al., 2006).

3.2.1. Contact time effects

As shown in Figs. 2a and 2b, the effects of the contact time on the methylene blue adsorption on the SSGS and BSSGS samples at room temperature were studied. The adsorption capacity and removal efficiency increased with increasing contact time. A comparison of the two samples revealed that they both reached equilibrium within 24 h, but they had different adsorption capacities. The SSGS sample had a higher adsorption capacity than the unactivated sample because of its porous structure (Li et al., 2006). The time required for the dye adsorption process to reach equilibrium was determined to be 24 h, and therefore, this time was selected as the optimal contact time. Remarkable removal efficiencies of 74.0% and 80.5% were observed within 2 h for the BSSGS and SSGS samples, respectively. The BSSGS sample exhibited an

**Fig. 1** The SEM morphology of surface image for SSGS sample.

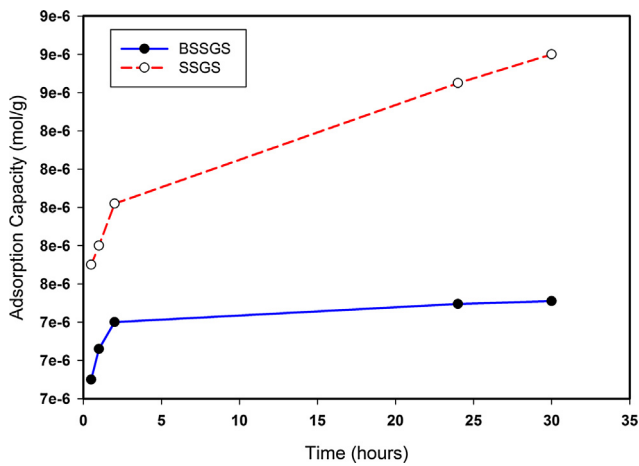


Fig. 2a Adsorption capacity of 10⁻⁵ M MB in different contact time.

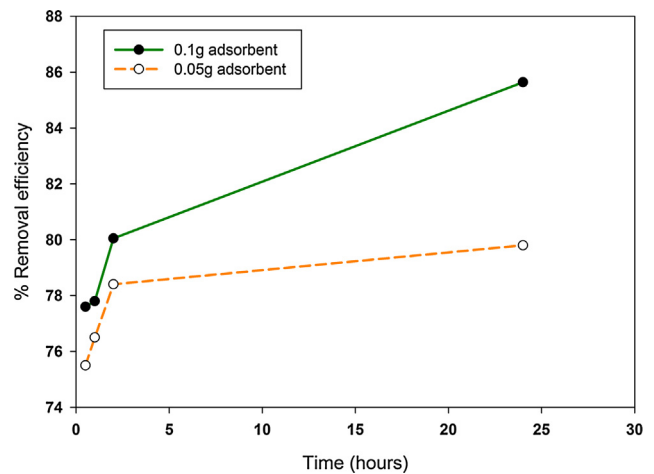


Fig. 3a Effect of adsorbent dosage (SSGS) on removal efficiency using 10⁻⁵ M of MB.

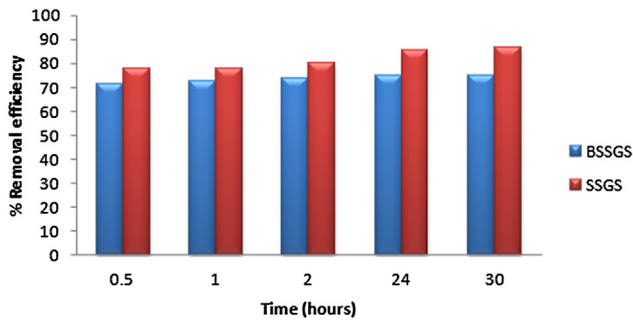


Fig. 2b Removal efficiency of 10⁻⁵ M MB in different contact time.

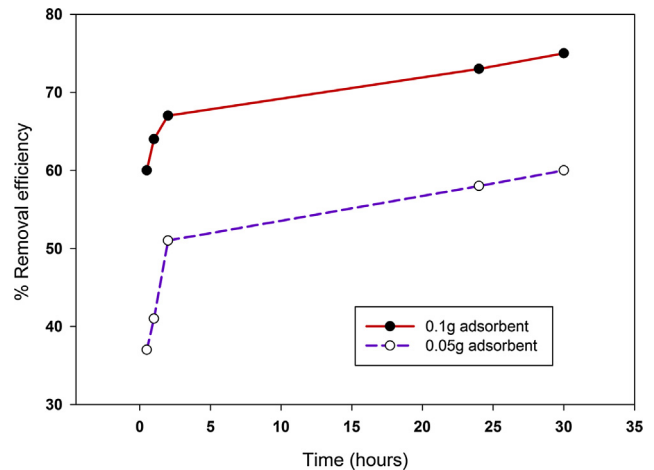


Fig. 3b Effect of adsorbent dosage (SSGS) on removal efficiency using 10⁻⁶ M of MB.

adsorption capacity of approximately 7.5×10^{-6} mol/g, whereas the SSGS adsorption capacity was 8.6×10^{-6} mol/g at equilibrium. Moreover, as shown in Fig. 2b, the removal efficiency of BSSGS varied from 71.6% to 75.1%, whereas the geopolymer sample exhibited higher removal efficiencies of 77.6–86.8%, due to the geopolymerization reaction.

3.2.2. Adsorbent dosage effects

When the MB concentration was 10⁻⁵ or 10⁻⁶ M, the removal efficiency increased with increasing adsorbent dosage. The adsorbent capacity for a given material is most significantly affected by the adsorbent dosage. Accordingly, the adsorbent dosage was optimized to achieve a consistent adsorption capacity. Increasing the adsorbent dosage from 0.05 g to 0.1 g resulted in increases in the dye removal efficiency from 79.8% to 85.6% for the 10⁻⁵ M MB solution and from 58% to 75% for the 10⁻⁶ M MB solution at equilibrium. Therefore, an adsorbent dosage of 0.1 g was used in the following experiments. As shown in Figs. 3a and 3b, the removal efficiency clearly varied with increasing adsorbent dosage. The observed increase could be explained by the available sorption sites on the geopolymer surface. In fact, increasing the amount of the geopolymer led to an increase in the dye adsorption from solution on the adsorbent material (Al-Zboon et al., 2011; Xu et al., 2008).

3.2.3. Initial dye concentration effects

The effects of the initial dye concentration on the removal efficiency were investigated using three different concentrations, as shown in Fig. 4. Clearly, the amount adsorbed increased as the methylene blue concentration increased from 10⁻⁶ M to 10⁻⁵ M (Mužek et al., 2014). The removal efficiencies were 85.6% and 73.0% for the 10⁻⁵ M and 10⁻⁶ M MB solutions, respectively. Moreover, the adsorption capacity also increased from 7.3×10^{-7} mol/g for the 10⁻⁶ M MB solution to 8.65×10^{-6} mol/g for the 10⁻⁵ M MB solution. It was concluded that more dye cations could be adsorbed from the 10⁻⁵ M MB solution because of the sufficient number of available pores in the adsorbent material; therefore, the adsorption capacity increased to a certain extent. However, at a higher concentration (10⁻⁴ M), the number of existing pores was not sufficient to adsorb the increased number of dye cations that were in the solution (Wang et al., 2007).

3.2.4. The effect of temperature

As shown in Fig. 5, the effects of the temperature on the adsorption capacity were considered. According to some

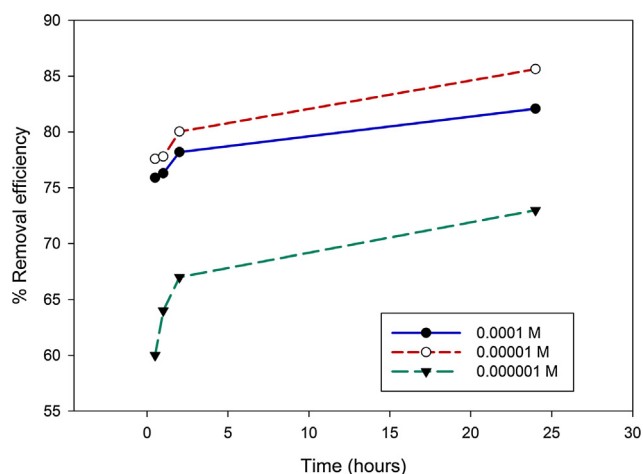


Fig. 4 The effect of different concentration (10^{-4} M, 10^{-5} M and 10^{-6} M MB) on removal efficiency of geopolymer sample.

reports, increasing the temperature increases the adsorption capacity (Buasri et al., 2008; Sindhunata et al., 2006; Wang et al., 2007). However, in this study, the MB removal efficiency decreased from 85.6% to 56.9% as the temperature was increased from 25 °C to 50 °C. The observed decrease was attributed to an exothermic process and enthalpy of adsorption (Li et al., 2006).

3.2.5. The effect of pH

One of the most important parameters in sorption processes is the pH. Changes in the solution pH affect the metal ion species that form in solution and can lead to inorganic compound formation. Indeed, the pH impacts the dye removal efficiency considerably (Lopez Guzman, 2014). As shown in Fig. 6, the effects of the pH on the MB adsorption capacity and dye removal were investigated. The removal efficiency decreased from 84.2% to 75.5% as the pH was increased from 3 to 8. The pH of the geopolymer solution in distilled water after 24 h of stirring was 9.49, demonstrating the strong basicity of the synthesized geopolymer used in this study. Furthermore, the geopolymerization reaction resulted in a negative solid surface charge (Davidovits, 1991; Hea et al., 2012). However, the pH of the SSGS geopolymer in the 10^{-5} M dye solution was

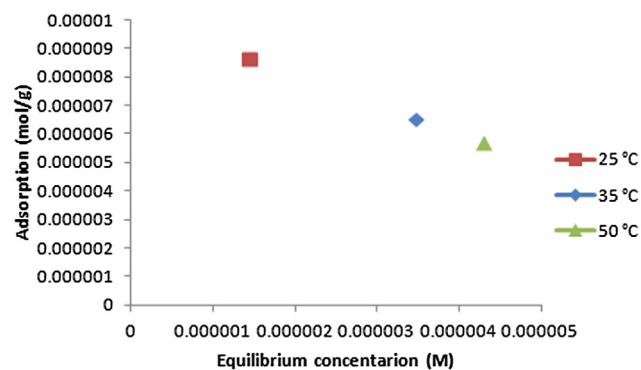


Fig. 5 MB adsorption on different equilibrium concentration at various temperatures.

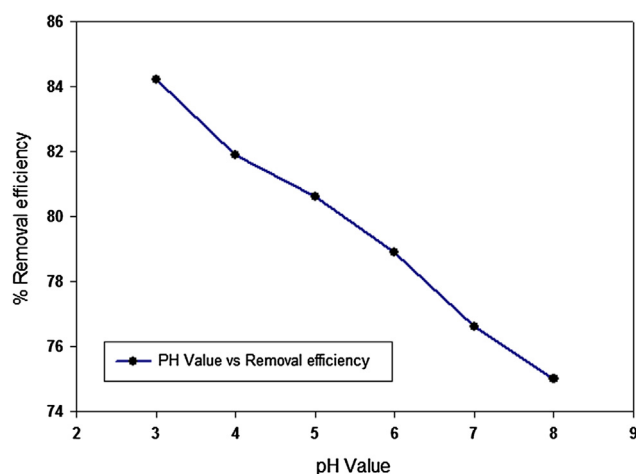


Fig. 6 Effect of different pH value on removal efficiency in 10^{-5} M of MB.

approximately 8.38 due to the cations in the methylene blue solution.

At pH 3, more positive charges exist at the adsorbent surface, which leads to hydroxyl group adsorption. The geopolymer sample exhibited a high dye removal efficiency at the low pH of 3, indicating that the zero point of charge occurs at a pH lower than 3. Increasing the pH resulted in lower removal efficiency due to the presence of fewer cations in the solution to adsorb at the negatively charged sites on the geopolymer surface. In addition, at higher pH values, the hydroxide ions hinder dye adsorption on the SSGS sample (Ayari et al., 2007; Xu et al., 2008). As expected, the minimum adsorption efficiency occurred at an alkaline pH. In fact, the decrease in the removal efficiency with increasing pH was due to adsorbent and adsorbate ionization, which led to repulsive forces between them. The oxygen functional groups at the geopolymer surface appear to play an important role in the dye adsorption process, and at pH values above 3, the bonds between the OH groups on the geopolymer surface increase, resulting in a negative surface charge (Moussavi, 2014).

3.3. Adsorption isotherms

The adsorption isotherm is an important factor for designing adsorption systems. In fact, adsorption isotherms can reveal adsorbent-adsorbate interactions. Therefore, these isotherms must be measured to determine and optimize the adsorbent capacity. Several isotherm models exist; of the equilibrium adsorption isotherms, the Langmuir single-layer and Freundlich multi-layer adsorption models are applicable to solid-liquid adsorption systems (Freundlich, 1906; Langmuir, 1916). Accordingly, in this study, the Freundlich and Langmuir adsorption models were fitted to the empirical equilibrium adsorption data. The coefficient of determination was used to demonstrate the fit of the regression equation to the sample data. The isotherm models were analysed by comparing the coefficients of determination (R^2) of the samples using the Excel software. The equilibrium adsorption isotherm data obtained using dye concentrations in the range of 10^{-6} – 10^{-4} M were fitted with the Freundlich equation. To analyse the isotherm models, different temperatures (25–50 °C) were

used with an adsorbent dosage of 0.1 g and the equilibrium contact time.

3.3.1. Langmuir adsorption

The Langmuir adsorption model assumes that adsorption occurs on a homogeneous adsorbent surface and successfully describes single-layer adsorption (Mohammad et al., 2010). Moreover, in the Langmuir adsorption model, it is assumed that only monolayer surface coverage occurs, all the surface

sites are equivalent, and the adsorbed molecules are immobile. The Langmuir adsorption model is expressed as follows (Eqs. (3) and (4)):

$$q_e = \frac{qmKLCe}{1 + KLCe} \tag{3}$$

$$\frac{C_e}{Q_e} = \frac{1}{qmKL} + \frac{1}{qm}C_e \tag{4}$$

where q_e is the amount of methylene blue adsorbed on the geopolymer surface at equilibrium, C_e is the MB equilibrium

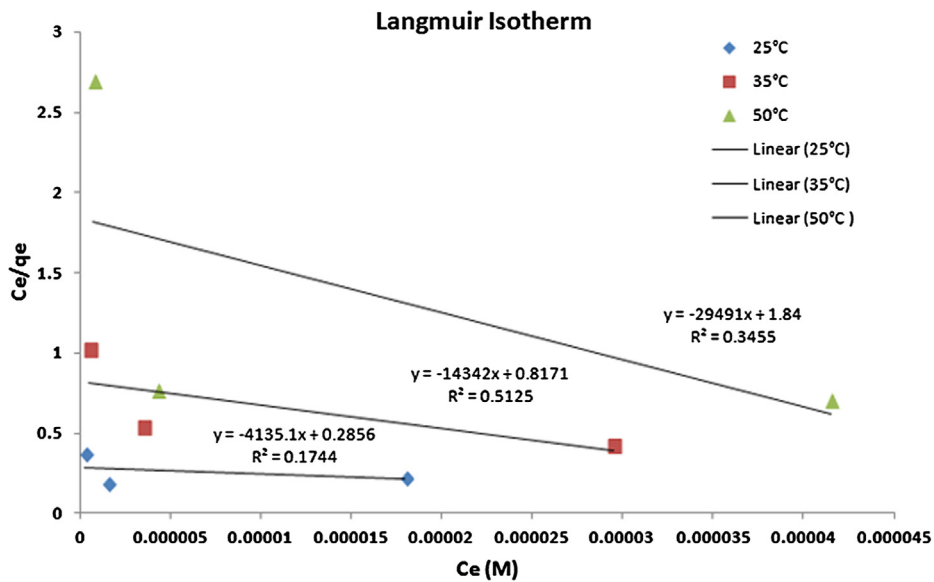


Fig. 7 Langmuir isotherm at different temperature (25–50 °C) and different concentration of MB solution (10^{-6} – 10^{-4} M) in pH 3 value.

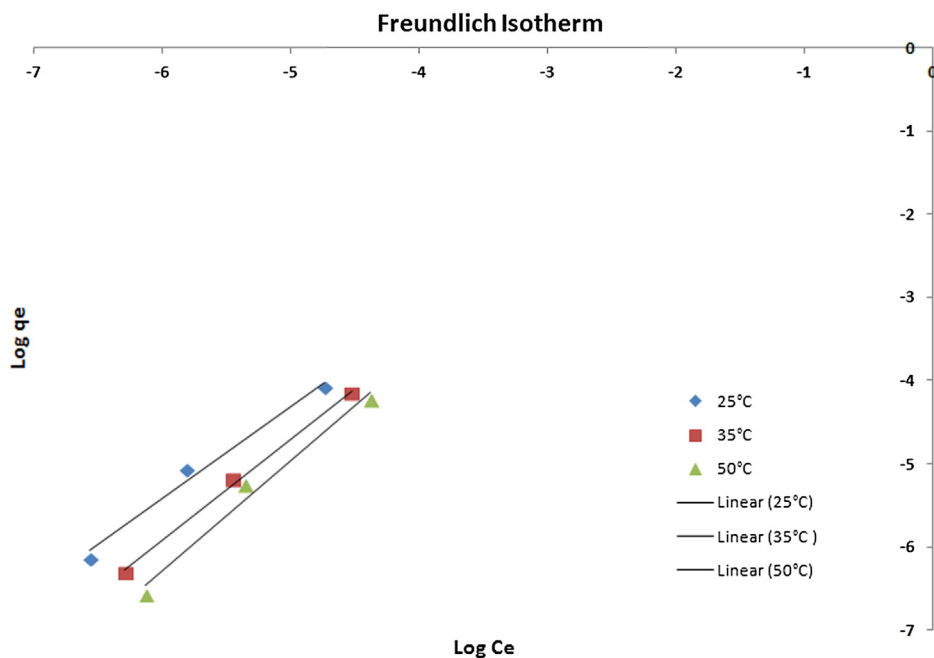


Fig. 8 Freundlich isotherm at different temperature (25–50 °C) and different concentration of MB solution (10^{-6} – 10^{-4} M) in pH 3 value.

Table 4 Some parameters of Freundlich isotherm in different temperature and pH value 3.

T (°C)	R ²	K _f	n
25	0.9825	2.5537	0.9017
35	0.9972	2.805	0.8210
50	0.9787	3.0307	0.7598

concentration (M), K_L is the Langmuir adsorption constant, and q_m is the maximum adsorption capacity of the adsorbent (mol/g). The adsorption capacity and Langmuir constant were obtained by linear regression and shown in Fig. 7. The Langmuir adsorption model was fitted to the data obtained using 10^{-6} – 10^{-4} M MB solutions at different temperatures. The slope of the Langmuir isotherm in Fig. 7 is clearly negative, indicating that the Langmuir single-layer model does not fit the equilibrium data, because of the non-uniform adsorption sites on the geopolymer surface and the interactions between the adsorbed molecules.

3.3.2. Freundlich isotherm

The Freundlich multi-layer adsorption model, which, unlike the Langmuir isotherm, describes heterogeneous systems (Adamson and Gast, 1967; Freundlich and Hatfield, 1926), was used to evaluate the obtained adsorption data. The Freundlich model was fitted to the data obtained using 10^{-6} – 10^{-4} M MB solutions at different temperatures and pH 3. The Freundlich isotherm applies to heterogeneous surfaces with non-uniform adsorption sites and is shown below (Eqs. (5) and (6)):

$$qe = K_f(Ce)^{1/n} \quad (5)$$

$$\log(qe) = \log(K_f) + \frac{1}{n} \log(Ce) \quad (6)$$

where K_f and n are the Freundlich isotherm constants, which correspond to the amount adsorbed and adsorption intensity, respectively, and can be calculated from the slope of the $\log q_e$ vs. $\log C_e$ plot. As shown in Fig. 8 and Table 4, the coefficients of correlation (R^2) for the fitted Freundlich isotherms are 0.9825, 0.9972, and 0.9787 for the equilibrium data collected in the temperature range of 25–50 °C. The R^2 value increases slightly as the temperature increases from 25 °C to 35 °C and then decreases when the temperature increases further to 50 °C. In addition, the good fit of the Freundlich isotherm model to the data might indicate that the good adsorption performance of the geopolymer might be due to the presence of non-uniform adsorption sites on its surface. Thus, the equilibrium data can be fitted by the Freundlich model.

4. Conclusions

A geopolymer paste was synthesized from green materials and used as an adsorbent for methylene blue dye removal. The synthesized geopolymer paste (SSGS) had a higher methylene blue removal efficiency than the unactivated mixed dry sample (BSSGS). Moreover, the adsorption conditions that could affect the adsorption capacity of the geopolymer paste were

optimized to obtain the maximum dye removal. The removal efficiency increased with increasing geopolymer dosage, contact time and temperature. The adsorption was studied at pH values in the range of 3–8, and the highest adsorption capacity was observed at pH 3. The amount of dye adsorbed increased with increasing initial methylene blue concentration in the range of 10^{-6} – 10^{-5} but decreased slightly at a higher concentration of 10^{-4} . The Freundlich isotherm describes the dye adsorption data well.

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