

Environmentally stable adsorbent of tetrahedral silica and non-tetrahedral alumina for removal and recovery of malachite green dye from aqueous solution

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Abstract

The conventional adsorbents like activated carbon, agricultural wastes, molecular sieves, etc., used for dye adsorption are unstable in the environment for long time, and hence the adsorbed dyes again gets liberated and pollute the environment. To avoid this problem, environmentally stable adsorbent of silica and alumina should be employed for malachite green adsorption. The adsorbents were characterized by Fourier transformed infrared spectroscopy (FT-IR) to confirm the tetrahedral framework of silica and non-tetrahedral framework of alumina. The adsorption equilibrium of dye on alumina and silica were 4 and 5 h, respectively, this less adsorption time on alumina might be due to the less activation energy on alumina ($63.46 \text{ kJ mol}^{-1}$) than silica ($69.93 \text{ kJ mol}^{-1}$). Adsorption increased with increase of temperature on silica, in alumina, adsorption increased up to 60°C , and further increase of temperature decreased the adsorption due to the structural change of non-tetrahedral alumina in water. The optimum pH for dye adsorption on alumina was 5 and silica was 6. The dye adsorptions on both adsorbents followed pseudo-second-order kinetics. The adsorption well matched with Langmuir and Freundlich adsorption isotherms and found that adsorption capacity on alumina was more than silica. The thermodynamic studies proved that the adsorption was endothermic and chemisorptions ($\Delta H^\circ > 40 \text{ kJ mol}^{-1}$) on alumina and silica. Recovery of dye on alumina and silica were studied from 30 to 90°C and observed that 52% of dye was recovered from alumina and only 3.5% from silica. The less recovery on silica proved the strong adsorption of dye on silica than alumina.

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Keywords: Malachite green; Adsorption; Thermal desorption; Tetrahedral silica; Non-tetrahedral alumina

1. Introduction

The organic dyes discharged (12%) from cosmetics, rubber, plastics, paper-manufacturing industries and textile dyeing industries are the main source for polluting surface water, ground water and soil [1,2]. To avoid this problem, the physico-chemical techniques like oxidation, flotation, coagulation, photochemical destruction and biodegradation were studied [3–8]. All these process required additional chemicals, which causes environmental pollution, corrosion and results the process was more expensive [3–8]. The fact necessitates to find out an environmentally stable adsorbent to uptake organic dyes from dye effluent.

Malachite green (MG) is a common (cationic) dye for dyeing wool, silk, leather, cotton, jute and fungicide, ectoparasiticide in aquaculture and fisheries [9,10]. Though it effectively controls the infection of bacteria, protozoans, cestodes, trematodes, nematodes and crustaceans in aquaculture [11], MG was found to cause muscle glycogenolysis, impairs protein synthesis, severe damage to gills and degenerative changes in fishes [12–14]. The dye MG is also harmful to symbiotic bacteria present in water and tumor promoter to human beings [15–19]. Biodegradation of MG was also studied by using some bacteria: *Kocuria rosea* MTCC 1532 [8]; fungi: *Fomes sclerodermeus*, *Phanerochaete chrysosporium* [20], *Trametes trogii* [21]; algae: *Cosmarium*, *Chlorella*, *Chlamydomonas* and *Euglena* [22]. The biodegradation of MG requires suitable condition for the growth of micro-organisms and was not effective for higher concentrations of dye [8,20–22]. Hence, it is an expensive and not a viable process for bulk dye effluent treatment.

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In adsorption methods, MG adsorption studies were already reported in rice husk-based carbon, activated carbon, bottom ash and hen feathers [23–25]. The activation of low cost adsorbents needs some chemical treatments that cause environmental pollution [26]. Activated carbon is an efficient adsorbent, but because of its high cost, the low cost adsorbents have more attention for dye removal. Moreover, the conventional adsorbents are environmentally unstable and hence they liberate dye again to the environment slowly after the adsorption. To avoid this problem, easily available, low cost and environmentally stable tetrahedral silica and non-tetrahedral alumina have been selected for this study. Based on literature survey, silica was used for adsorption of Astrazone blue, Basic blue 3, Basic red 22, Acid blue 25 [2,27]. Alumina was used as adsorbent for Crystal Violet [28,29]. To our knowledge, no work was reported for adsorption of MG on silica and alumina. Hence, we attempted to study the possibility of using tetrahedral silica and non-tetrahedral alumina as an adsorbent for removal of MG from wastewater.

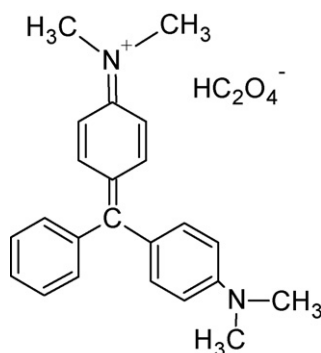
2. Experiment

2.1. Physico-chemical characterization

FT-IR spectrum of the silica and alumina were recorded in Nicolet (Avatar 360) FT-IR spectrophotometer using KBr pellet technique. About 15 mg of the sample was pressed into a self-supported wafer of 13 mm diameter. This pellet was used to record the infrared spectra in the range 4000–400 cm^{-1} .

2.2. Activation of adsorbents and dye solution preparation

The silica gel and alumina (both are column grade supplied by Merck India Ltd.) were activated before the adsorption experiment at 150 °C for 3 h in hot-air oven. The required amount of adsorbents was taken from this activated adsorbent for all the experiment. The malachite green oxalate (chemical name *N,N,N',N'*-tetramethyl-4,4'-diaminotriphenylcarbenium oxalate) purchased from Merck (microscopy grade) India Ltd. was used for adsorption studies (chemical formula $(\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}_2)_2 \cdot 2\text{C}_2\text{H}_2\text{O}_4$, molecular weight 837.02, C.I. No. 420000 and λ_{max} 616–620 nm) (Scheme 1).



Scheme 1. Structure of malachite green.

The stock solution 1000 mg l^{-1} was prepared by dissolving 1 g of dye in 1 l of double distilled water in a standard measuring flask. The desired concentrations were prepared by successive dilution of the stock solution. The dye concentration was analyzed with UV–vis spectrophotometer [Elico-model-SL171].

2.3. Adsorption experiment

Adsorption studies were carried out by adding 0.25 g of activated alumina and silica separately in 50 ml of dye solution in a 100 ml conical flask. The mixtures were stirred on a Magnetic stirrer (Remi-Model-1 MLH) separately. At the end of the experiment, the solutions were centrifuged off and final concentrations of solution were measured by spectrophotometrically at 617 nm. The amount of MG adsorbed on adsorbent was obtained from the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where Q_e is the amount of dye adsorbed (mg g^{-1}), C_0 and C_e are the initial and equilibrium liquid-phase concentrations of MG (mg l^{-1}), respectively, V is the volume of solution (l) and W is the amount of adsorbent (g).

The contact time was studied up to 10 h to find out the equilibrium adsorption time. The concentration (50–300 mg l^{-1}) effect of MG adsorption on silica and alumina were studied at room temperature. The temperature effect of MG adsorption on silica and alumina were studied from 30 to 90 °C. The dosage of silica was studied in the range of 50–450 mg and dosage of alumina was studied in the range 150–550 mg. The pH effects of MG adsorption were studied in the pH range 3–7 using 300 mg l^{-1} (pH 4) MG solution. Altering the pH above and below 4 were carried out by adding 0.1N NaOH or 0.1N HCl. The pH was measured by using pH meter, Elico-model LI 613.

2.4. Adsorption kinetics and isotherms

The adsorption kinetics of MG on alumina and silica were studied at temperature range 30–50 °C. The adsorption rates were monitored with 10-min interval and the rate constant of adsorption was calculated by using pseudo-second-order kinetics equation given as below:

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{1}{Q_e t} \quad (2)$$

where k is the rate constant, Q_e and Q_t are the amounts of dye adsorbed (mg g^{-1}) at equilibrium and time t (min), respectively.

MG adsorption isotherm data were collected at different concentrations (50–300 mg l^{-1}) at pH 6 and at room temperature for silica and alumina. The data were fitted with Langmuir and Freundlich adsorption isotherms.

The Langmuir equation is represented as

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}} K_L} + \frac{C_e}{Q_{\text{max}}} \quad (3)$$

where Q_e is the equilibrium dye concentration on the adsorbent (mg g^{-1}), C_e is the equilibrium dye concentration in solution

(mg l^{-1}), Q_{max} is the monolayer capacity of the adsorbent (mg g^{-1}) and K_L is the Langmuir constant (l g^{-1}).

The Freundlich equation is represented as

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where Q_e is the equilibrium dye concentration on the adsorbent (mg g^{-1}), C_e is the equilibrium dye concentration in solution (mg l^{-1}), K_F is the Freundlich constant (l g^{-1}) and n (dimensionless) is the heterogeneity factor.

2.5. Dye recovery

The recovery of adsorbed MG from silica (14.9 mg g^{-1}) and alumina (37.8 mg g^{-1}) were studied from 40 to 90°C in the presence of water. The λ_{max} and concentration of recovered dye were measured by spectrophotometer.

3. Results and discussion

3.1. Physico-chemical characterization

3.1.1. FT-IR spectra of silica

FT-IR of silica (Fig. 1) was shown a band at 1106 cm^{-1} asymmetric stretching of Si–O–Si tetrahedral and corresponding symmetric stretching was observed at 674 cm^{-1} [30]. The Si–O–Si bending mode was positioned at 466 cm^{-1} . The peak at 3423 cm^{-1} was due to uncondensed –OH groups and water molecules present in silica.

3.1.2. FT-IR spectra of alumina

The FT-IR spectrum of alumina was shown in Fig. 2. The band observed at 1605 cm^{-1} might be the Al–O–Al asymmetric stretching and corresponding symmetric stretching was observed at 606 cm^{-1} . The broad peak at 3455 cm^{-1} was due to uncondensed –OH groups and weak band observed at 3779 cm^{-1} might be due to adsorbed water molecules present in alumina.

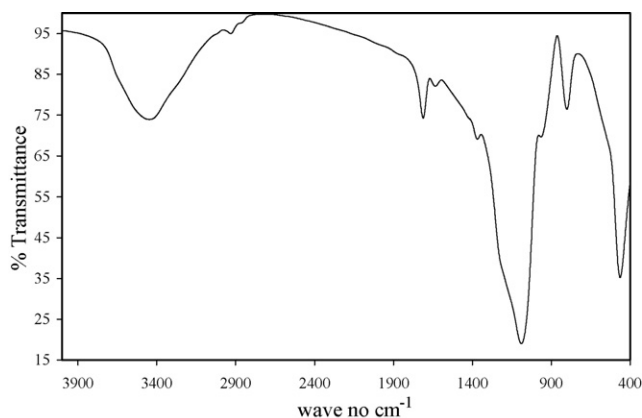


Fig. 1. FT-IR spectrum of silica.

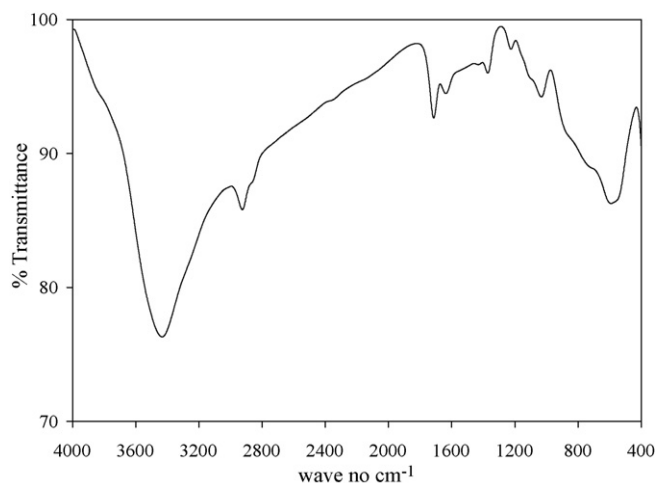


Fig. 2. FT-IR spectrum of alumina.

3.2. Effect of contact time

The equilibrium adsorption times were studied on silica and alumina in 100 mg l^{-1} MG solution (Fig. 3). The other adsorption parameters like temperature, pH and dosage of adsorbent were fixed constant for both adsorbents. The maximum adsorption equilibrium was observed at 4 h for alumina and 5 h for

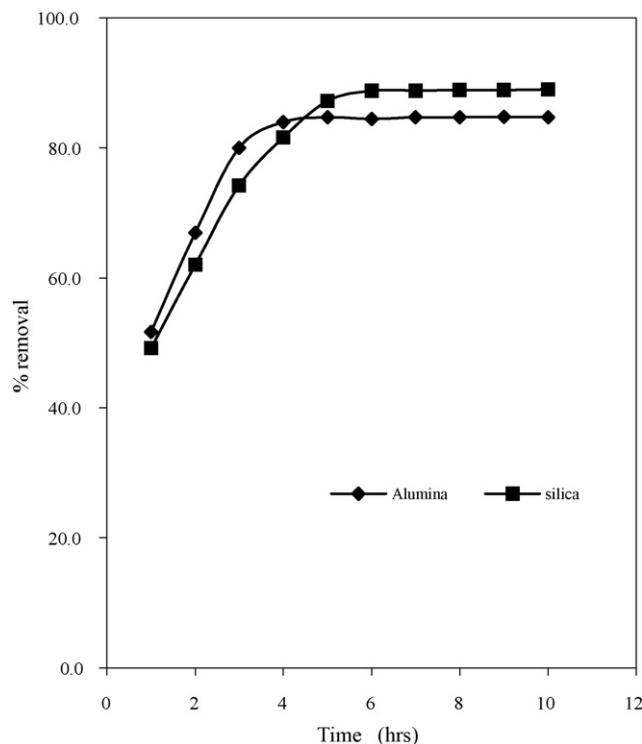


Fig. 3. Effect of contact time for MG adsorption on silica and alumina: temperature— 30°C ; dosage— 250 mg ; concentration— 100 mg l^{-1} . The standard deviation of MG adsorption on silica for the contact time of 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 h are 0.7162, 0.7530, 0.4087, 0.6269, 0.8843, 0.7797, 0.6083, 0.6083, 0.6731 and 0.6140, respectively. The standard deviation of MG adsorption on alumina for the contact time of 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 h are 0.3916, 0.3512, 0.5447, 0.8995, 0.7805, 0.6185, 0.6481, 0.6500, 0.6500 and 0.6500, respectively.

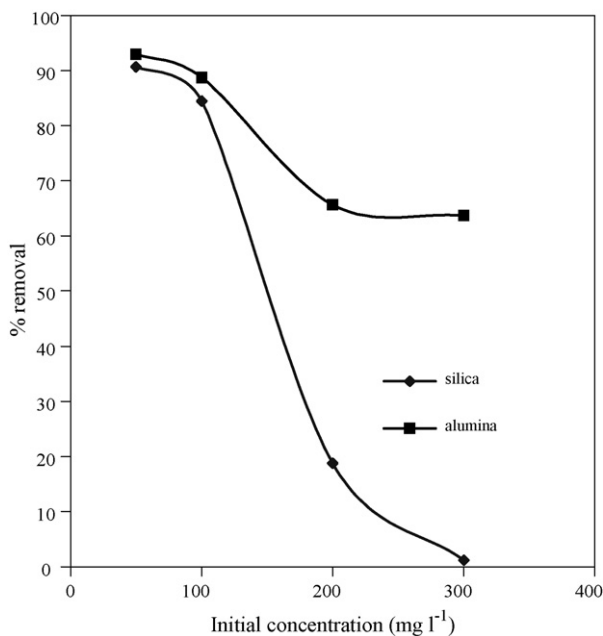


Fig. 4. Concentration effect on MG adsorption: temperature—30 °C; dosage—250 mg; contact time—silica: 5 h, alumina: 4 h. The standard deviation of MG adsorption on silica for the concentration of 50, 100, 200 and 300 mg l⁻¹ are 0.3194, 0.4123, 0.3391 and 0.2168, respectively. The standard deviation of MG adsorption on alumina for the concentration of 50, 100, 200 and 300 mg l⁻¹ are 0.2588, 0.2074, 0.2449 and 0.2408, respectively.

silica. This time difference between the two adsorbents to attain maximum adsorption was due to the nature of the adsorbents. Alumina has more electron-withdrawing tendency than silica due to the presence of Lewis acid sites in it. Hence, the adsorption was faster in alumina than silica. This was proved in the activation energy (E_a) calculation that the alumina E_a was lesser than silica E_a (Table 3). The less E_a of alumina indirectly mean that the electron-withdrawing tendency of alumina reduced the energy barrier between the solid and liquid interfaces. Then entropy of adsorption of MG on silica was more than alumina (Table 3). This less activation energy and entropy leads to fast adsorption and hence adsorption contact time on alumina was less than silica.

3.3. Effect of concentration of dye

The concentration effect of MG (50–300 mg l⁻¹) for maximum uptake had been studied on silica and alumina at constant temperature and adsorbents dosage. The adsorption percentage was found to decrease with increase of MG concentration (Fig. 4). This was attributed to decrease of natural pH of dye solution with increase of dye concentration (Table 1). In the pH study, it was proved that the dye adsorption decrease with decrease of initial dye pH below 4 (Fig. 6). In addition, increase the dye concentration of MG; surface area and active sites of the adsorbent were saturated. Hence, adsorption decreases with increase of dye concentration.

The initial and final pH of MG dye solutions (50–300 mg l⁻¹) were measured before and after the adsorption process. The pH measurements shown that the increase of dye adsorption

Table 1
pH changes for the MG adsorption on silica and alumina

Adsorbents	Concentration (mg l ⁻¹)	Initial pH	Final pH	Removal (%)
Silica	50	4.74	6.92	90.7
	100	4.64	6.85	87.0
	200	4.50	5.37	18.8
	300	3.93	4.09	1.2
Alumina	50	4.75	6.98	93.0
	100	4.70	6.90	89.5
	200	4.45	5.89	65.6
	300	3.97	5.75	63.7

increases the aqueous solution pH nearer to 7.0 (Table 1). Hence, this adsorption process did not affect the water quality.

3.4. Effect of temperature

The effects of temperature on the removal of MG were studied in the range of 30–90 °C (Fig. 5). In alumina, the adsorption increases up to 60 °C and further increase of temperature decreases the adsorption (Scheme 2). Below 60 °C, water adsorption on alumina increases the active sites of alumina for more dye adsorption (Scheme 3). Above 60 °C, the hydrated water desorbed from alumina leads to reduce the active sites of MG adsorption (Scheme 4). Hence, the adsorption below 60 °C increases and above 60 °C decreases. However, in silica, there was no hydration and structural change with temperature due to its tetrahedral framework. The MG adsorption on silica was

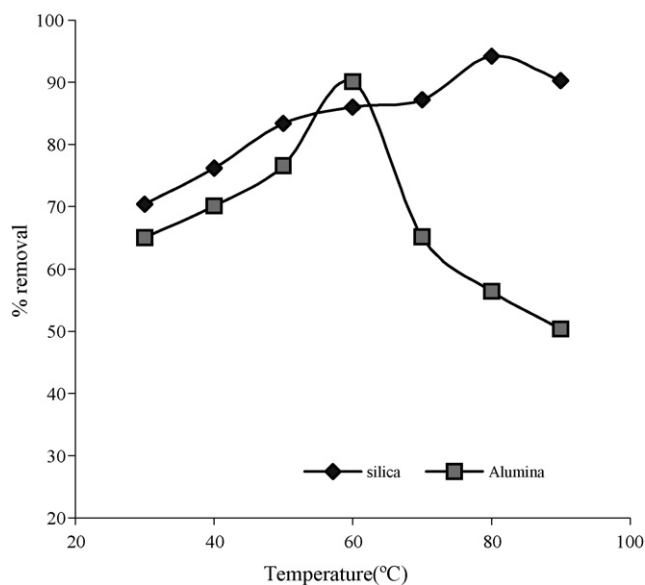
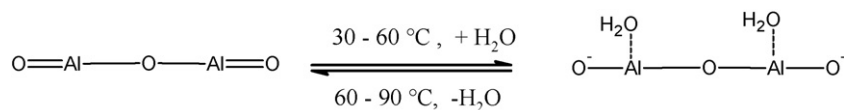
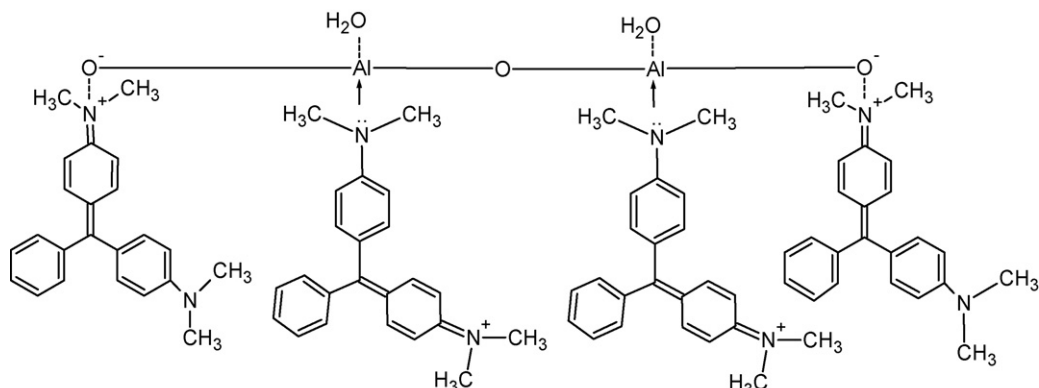


Fig. 5. Temperature effect of MG adsorption on alumina and silica; dosage—250 mg; concentration—100 mg l⁻¹; contact time—silica: 5 h, alumina: 4 h. The standard deviation of MG adsorption on silica for the temperature of 30, 40, 50, 60, 70, 80 and 90 °C are 0.2408, 0.1673, 0.2074, 0.1581, 0.2881, 0.1673 and 0.2074, respectively. The standard deviation of MG adsorption on alumina for the temperature of 30, 40, 50, 60, 70, 80 and 90 °C are 0.2168, 0.1581, 0.1517, 0.1140, 0.1140, 0.0548 and 0.1140, respectively.



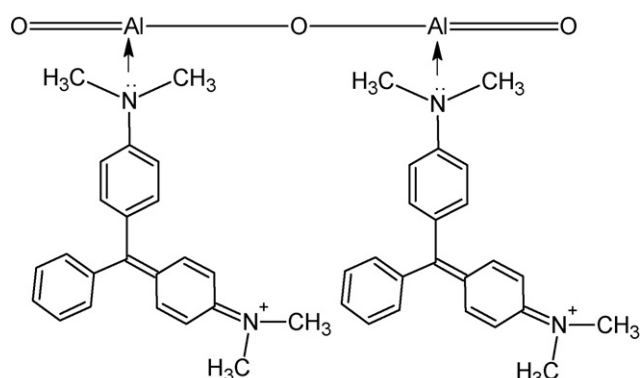
Scheme 2. Hydration and dehydration of alumina.

Scheme 3. Adsorption of MG on Al and O⁻ sites of alumina below 60 °C.

through positive and negative charge interaction between MG and silica (Scheme 5). The adsorption of MG on silica gradually increases with increase of temperature due to the strong interaction between MG and silica.

3.5. Effect of pH

The effect of initial pH of MG adsorption on alumina and silica were studied in the range 3–7 (Fig. 6). In silica, the dye uptake was maximum 99% in the pH range 5–7 and at pH 4 adsorption was 20%. The maximum adsorption on silica at pH 5–7 may be due to the development of high negative charge on the silica surface and low adsorption (20%) at pH 4 may be due to the point of zero charge of silica [31]. In alumina, the adsorption increases gradually with increase of pH and reach the maximum adsorption at pH 6. The low adsorption below pH 4 may be due to the protonation of amino groups of dye, the protonated amino group did not adsorb on electron deficient aluminum active sites. Hence, adsorption decreases with decrease of pH below 4.



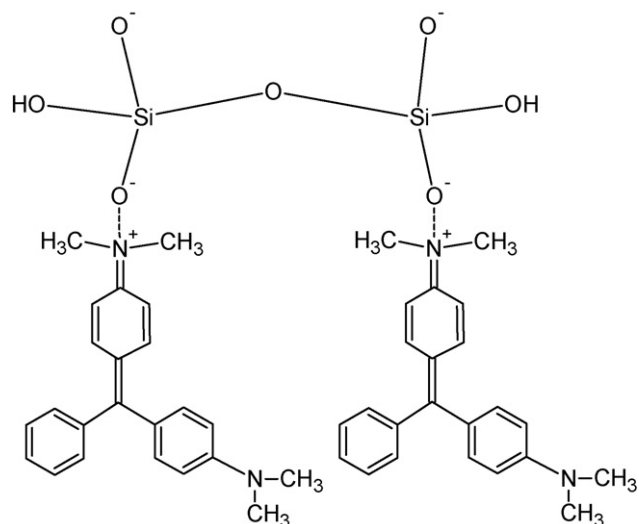
Scheme 4. Adsorption of MG on aluminum sites alone above 60 °C.

3.6. Effect of dosage

The effect of silica and alumina dosage (150–450 mg) for the adsorption of MG were studied and observed that the percentage removal of the dye was found to increase with increase of adsorbent dosage (Fig. 7), since the increase of dosage increases the surface area and active sites for more adsorption of MG on alumina and silica. The optimum dosage of silica was 150 mg for 50 ml of 100 mg l⁻¹ MG solution and for alumina was 250 mg for 50 ml of 200 mg l⁻¹ dye solution.

3.7. Adsorption isotherms

The MG adsorption isotherm data at different concentrations at pH 7 were collected. These data were well fitted with Langmuir and Freundlich adsorption isotherms (Figs. 8 and 9). The



Scheme 5. Adsorption of MG on silica.

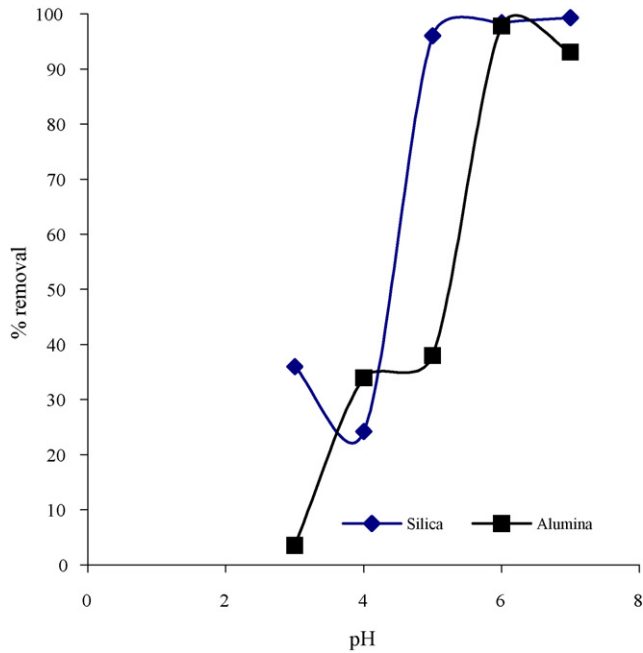


Fig. 6. Effect of pH on adsorption of MG on silica and alumina: temperature—30 °C; dosage—250 mg; concentration—300 mg l⁻¹ and contact time—silica: 5 h, alumina: 4 h. The standard deviation of MG adsorption on silica for the pH of 3, 4, 5, 6 and 7 are 0.1581, 0.1817, 0.1483, 0.1924 and 0.2121, respectively. The standard deviation of MG adsorption on alumina for the pH of 3, 4, 5, 6 and 7 are 0.1140, 0.8871, 0.2702, 0.2608 and 0.1924, respectively.

R² values and Freundlich constant (*n*) obtained from Langmuir and Freundlich adsorption isotherms of silica and alumina were given in Table 2. The Freundlich constant *n* was greater than 2 had shown the favourability of MG adsorption on alumina and silica [32].

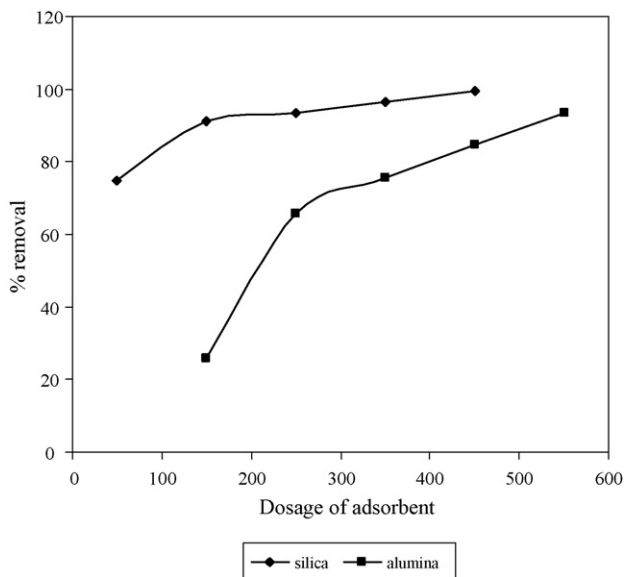


Fig. 7. Effect of adsorbent dosage on MG adsorption: temperature—30 °C; silica: contact time—5 h, concentration—100 mg l⁻¹; alumina: contact time—4 h, concentration—200 mg l⁻¹. The standard deviation of MG adsorption on silica for the dosage 50, 150, 250, 350 and 450 mg are 0.2167, 0.1095, 0.2073, 0.1870 and 0.2280, respectively. The standard deviation of MG adsorption on alumina for the dosage 150, 250, 350, 450 and 550 mg are 0.2549, 0.2236, 0.3000, 0.2949 and 0.1673, respectively.

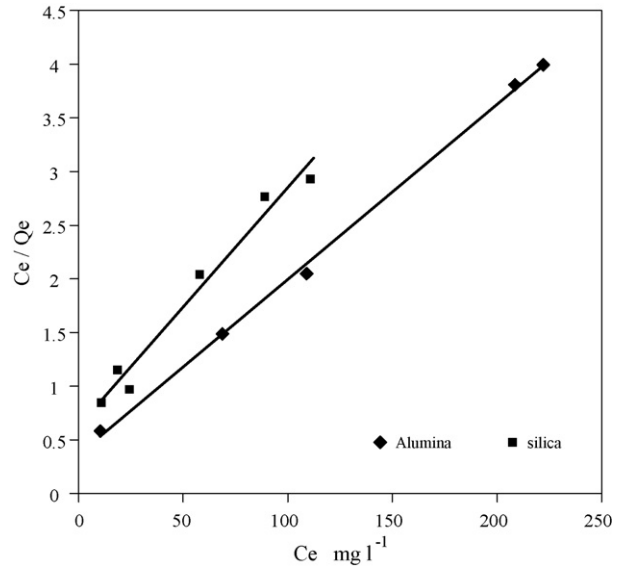


Fig. 8. Langmuir adsorption isotherms of MG on silica and alumina.

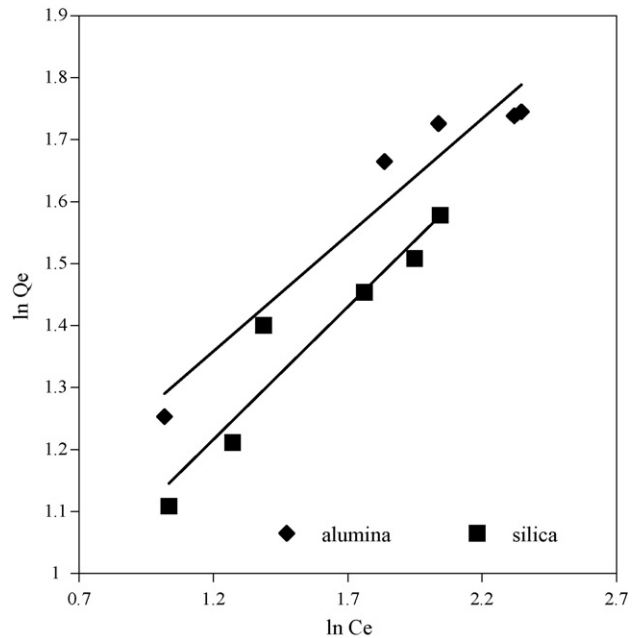


Fig. 9. Freundlich adsorption isotherms of MG on silica and alumina.

3.8. Adsorption kinetics

The adsorption kinetics of MG on alumina and silica have been studied between 30 and 60 °C. The rate constant (*k*) was calculated by using pseudo-second-order kinetic equation. The

Table 2

Langmuir and Freundlich adsorption isotherm parameter of MG on silica and alumina

Adsorbents	Langmuir isotherm			Freundlich isotherm		
	Q _{max}	K _L	R ²	K _F	<i>n</i>	R ²
Silica	45.05	0.0354	0.9724	8.1040	2.3375	0.9125
Alumina	61.35	0.0447	0.9985	5.0431	2.6667	0.9310

Temperature 30 °C.

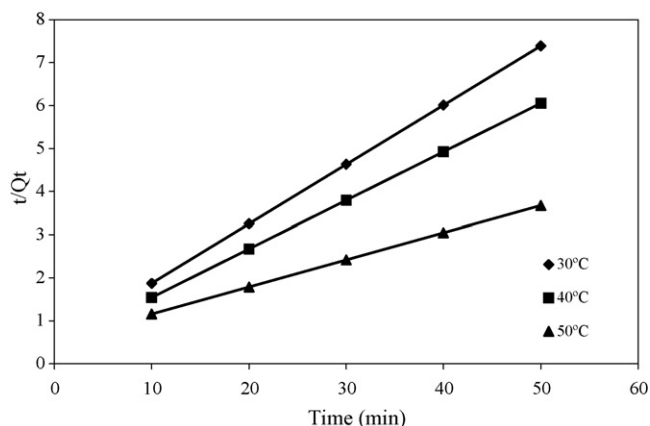


Fig. 10. The pseudo-second-order kinetics plots for adsorption of MG on silica.

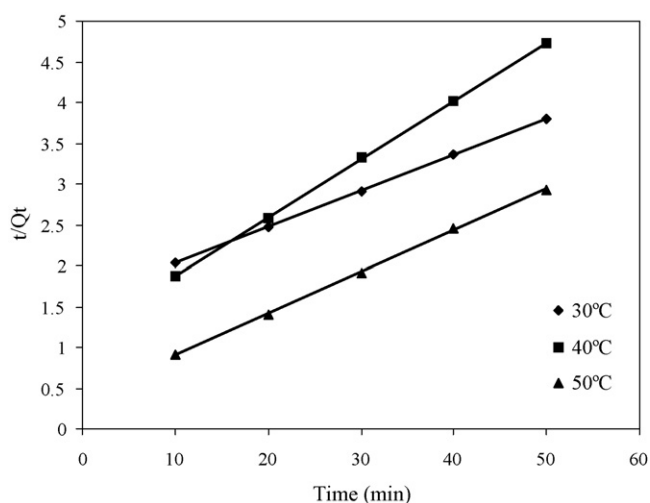


Fig. 11. The pseudo-second-order kinetics plots for adsorption of MG on alumina.

plot of t/Q_t versus t gives straight lines for MG adsorption on alumina and silica (Figs. 10 and 11). The linear regression coefficients higher than 0.99 indicate that the adsorption followed the pseudo-second-order kinetics.

3.9. Adsorption thermodynamics

Free energy (ΔG°) of adsorption was calculated by using the following equation:

$$\Delta G^\circ = -RT \ln K^* \quad (5)$$

where K^* is equilibrium constant of adsorption. The equilibrium constant is calculated from the following equation [33]:

$$k = \frac{k_B T}{h} K^* \quad (6)$$

where k is rate constant calculated from the pseudo-second-order rate equation and k_B and h are Boltzmann's and Planck's constant, respectively.

Enthalpy (ΔH°) of MG adsorption was calculated by using the following equation:

$$\Delta H^\circ = E_a - RT \quad (7)$$

The activation energy (E_a) for adsorption of MG on alumina and silica were calculated from the rate constant by using Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (8)$$

where A is the Arrhenius frequency factor, R is the gas constant

Entropy (ΔS°) of MG adsorption was calculated from ΔG° and ΔH° values by using the following equation:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (9)$$

The ΔG° , ΔH° and ΔS° values calculated for the adsorption of MG on alumina and silica were given in Table 3. The positive ΔH° greater than 40 kJ mol⁻¹ indicate that the adsorption was endothermic and chemisorption [34]. The negative ΔS° values indicate the dye molecules were orderly adsorbed on alumina and silica surfaces.

3.10. Recovery of MG

Recovery of MG from silica and alumina were carried out with water in the temperature range of 40–90 °C (Fig. 12). It was found that desorption of MG on alumina increases with increase of temperature and found that 52% of dye was recovered at 90 °C, but desorption from silica in water was very low (3.47%). The very low desorption observed in water (3.47%), indicates that the MG had more affinity on silica than water. This fact proved that the MG pollutes the soil to a maximum extent than water. The recovered dye characterized by spectrophotometrically and observed that the λ_{\max} for the recovered dye was 618 nm, which was within the range of original dye λ_{\max} 616–620 nm. This confirms that there was no change in MG structure during the recovery process.

Table 3
Thermodynamic parameters for the adsorption of MG on silica and alumina

Adsorbent	Temperature (°C)	Activation energy (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
Silica	30	69.93	82.43	60.94	-70.94
	40		85.83	60.85	-79.82
	50		92.45	60.77	-98.10
Alumina	30	63.46	91.09	64.41	-88.05
	40		90.89	64.33	-84.87
	50		92.89	64.24	-88.67

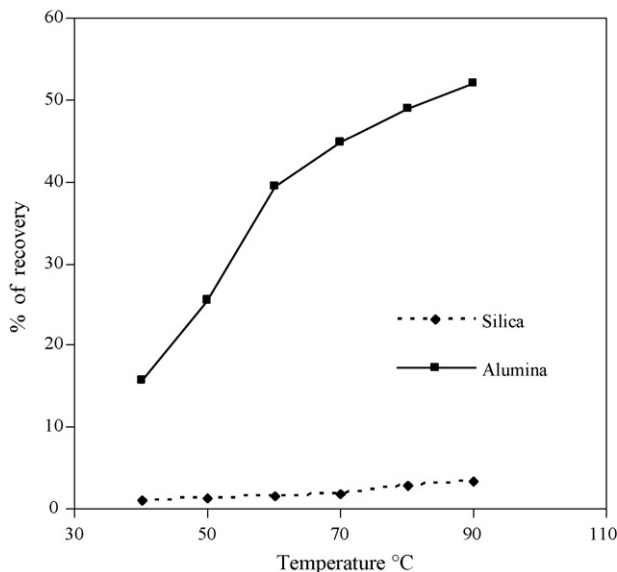


Fig. 12. Recovery of MG from silica and alumina at various temperatures in water.

4. Conclusion

The adsorption equilibrium attains at 4 h on alumina and 5 h on silica. The optimum dye uptake pH on alumina and silica was 6 and 5, respectively. The MG adsorption on silica increases with increase of temperature up to 80 °C. The adsorption of MG on alumina increases up to 60 °C and further increase of temperature decrease the dye adsorption. The uptake of MG on alumina decreases 93.0–63.7% and on silica decreases 90.7–1.2% with increases of concentration from 50 to 300 mg l⁻¹. The MG removal increased from 74 to 99% on silica and 26 to 93.4% on alumina with increase of adsorbents dosage from 150 to 550 mg. Moreover, the pH of solution after the maximum adsorption was nearer to water pH. Thus, the adsorption process proved that the water pH was not affected by using silica and alumina as an adsorbents. The adsorption data well matched with Langmuir and Freundlich adsorption isotherm model and pseudo-second-order kinetic equation proved that adsorption was multilayer and follow pseudo-second-order kinetics. The enthalpy of adsorption on silica and alumina are +60 and +64 kJ mol⁻¹, respectively. This value proved that the adsorption was chemisorption and endothermic. Recovery of MG from alumina and silica were 52 and 3.5% respectively. The poor desorption of MG from silica proved that it adsorbed more strong and stable than alumina, but 52% of MG recovery from alumina proved that it is a better adsorbent for MG adsorption and recovery from dye effluent.

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