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Synthesis of poly GMA/DVB and its application for the removal of Malachite Green from aqueous medium by adsorption process

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ABSTRACT

In the present study, poly glycidyl methacrylate/divinyl benzene has been synthesized by the co-polymerization of glycidyl methacrylate and divinyl benzene monomers by thermal polymerization method and used as an adsorbent for the removal of malachite green (MG) dye from aqueous medium. This polymeric adsorbent is characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, and Fourier transform infrared spectroscopy. The adsorption data has been applied to various isotherm models such as Langmuir, Freundlich, Dubinin–Radushkevich (D–R), Flory–Huggins (F–H), and Temkin models. Different adsorption parameters such as time variation, effect of dye concentration, and pH effect is successfully evaluated. The maximum adsorption capacity is found to be 13.6 mg g^{-1} at 310 K which is higher than some other adsorbents reported earlier. In order to study the adsorption mechanism, different kinetic models namely pseudo-first-order, pseudo-second-order and intra-particular diffusion model are applied and it is found that adsorption of MG on to polymer adsorbent follow pseudo-second-order kinetics. The change in Gibbs free energy (ΔG) was also calculated. The high removal capacity of present adsorbent indicate that it can be used as a promising and effective adsorbent for the removal of MG from aqueous medium.

Keywords: Malachite green; Poly GMA/DVB; Adsorption capacity; Freundlich isotherm; Scanning electron microscopy

1. Introduction

Save water to save our planet and to make the future of human safe is what we need now. During last decade, environmental pollution has become a major area of concern due to large industrial growth and increase in human population. Soil, water, and air quality have been badly affected due to human activities. Water pollution is one of the major threats for the modern world. Removal of chemical pollutants such as heavy metals, pesticides, and industrial dyes from the wastewater is still a matter of active ecological research. Industrial effluents are one of the major causes of environmental pollution because effluents discharged from industries are highly colored with a large amount of suspended organic solids [1].

Dyes and pigments are being extensively used in textile, plastic, food, leather, paper, printing,

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pharmaceutical, and cosmetic industries for coloring purpose [2]. Approximately, 0.7 million tons of 10,000 different dyes are produced every year for various industrial processes [3]. About two-third of the total produced dyes is used by the textile industry and a considerable percentage of these dyes is discharged into the effluents during dying process, about 10–15% of the dyes used come out through the effluents [4]. Textile effluents of these dyes are highly toxic or even carcinogenic and mutagenic, as they contain a large number of metal complex dyes [5,6]. The discharge of dye colored wastewaters into the aquatic ecosystem cause environmental as well as public health problem because of the negative ecotoxicological effects and bioaccumulation in wildlife [7]. Many dyes present in wastewater can decompose into aromatic amines under aerobic conditions which are carcinogenic and can cause serious problems to humans and animal health [8,9]. Dyes can cause many diseases such as allergy, dermatitis, skin irritation, and cancer in humans [10]. Also, color in surface water affects photosynthesis because it prevents light penetration, which is a harmful effect to aquatic life [11].

Malachite green (MG), N-methylated diaminotriphenyl methane, also known as basic green 4 (Fig. 1(a)) is a basic, cationic dye and most widely used for the dyeing purpose amongst the other dyes in leather, wool, silk, cotton, paper, distilleries, jute, paper, as a food coloring agent, and food additive [12]. MG is also used as antibacterial, antifungal, and antiseptic in aquatic environment and to control fish parasites [13]. Discharge of MG into the hydrosphere can cause environmental degradation as it gives undesirable color to water and reduces sunlight penetration. The consumption of MG has many adverse effects due to its carcinogenic, genotoxic, mutagenic, and teratogenic properties [14]. The carcinogenic properties of MG are due to the presence of the nitrogen [15]. MG is highly cytotoxic to mammalian cells and also acts as a liver tumor-enhancing agent [16]. MG when discharged into water streams, it affects the aquatic life and causes detrimental effects in liver, gonads, gill, kidney, intestine, and pituitary gonadotrophic cells [17]. It decreases food intake capacity, growth and fertility rates; causes damage to liver, spleen, heart, inflicts lesions on skin, eyes, lungs, and bones [18].

Therefore, it is of prime importance to develop a reliable method for the removal of this hazardous dye from the wastewater. Different physical, chemical, and biological methods are being employed for the removal of MG from the wastewater, such as coagulation, chemical oxidation, membrane separation process reverse osmosis, electrochemical processes, aerobic and anaerobic microbial degradation [18], flocculation, adsorption, ozonation, fungal decolonization, ion

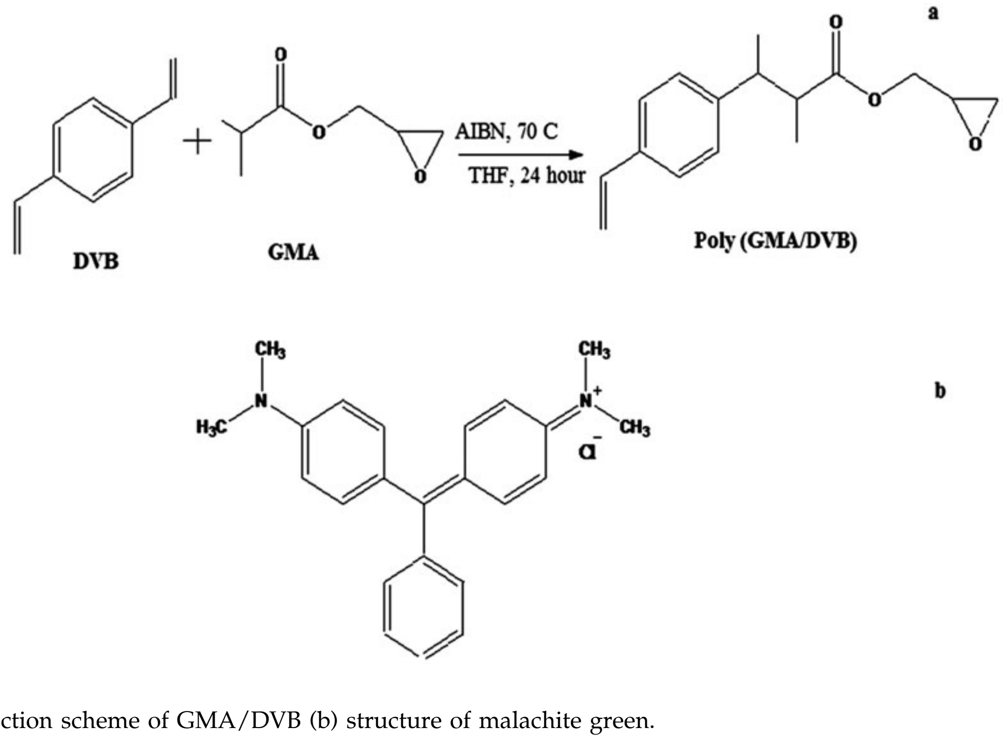

Fig. 1. (a) Reaction scheme of GMA/DVB (b) structure of malachite green.

exchange, electrodialysis, ultracentrifugation, and chemical precipitation, integrated iron(III) photoassisted-biological treatment, integrated chemical-biological degradation, solarphoto-Fenton, and biological processes, and Fenton-biological treatment scheme [19]. Among all these, adsorption has been found to be the most efficient and effective in removing organic and inorganic pollutants due to its low cost, better efficiency, ease of operation, environmental benignity, and complete removal of pollutants even from very dilute solutions [20].

A variety of adsorbents has been reported for the removal of MG from the industrial effluents such as chitosan, ground charcoal, ground shrimp skeleton, soil, activated carbon, ground oyster shell, de oiled soya, micro algae, tri-sylsilicas, silica gel [21], bagasse fly ash, clay, olive stone, saw dust, red mud, marine sediment, hazelnut shells, moss carbon nanotubes, marine algae, seashells, fly ash [22], oil palm trunk fiber, pomelo (*Citrus grandis*) peel, sunflower seed hull, durian peel, water hyacinth, water hyacinth of Baker's yeast [23], rattan sawdust, ginger waste, maize cob (*Zea maize*), lemon peel, tamarind fruit shell, hen feathers, raw barley straw, silica–zirconia mixed oxide, eggshell, TiO_2/AC, granular kohlrabi peel, akash kinari coal, orange waste, and granular kohlrabi peel [24].

The objective of the present work is to study the adsorption capacity and mechanism of MG onto poly GMA/DVB. The synthesis of polymeric adsorbent is also reported in the present work. Furthermore, effect of adsorbent dosage, initial MG concentration, effect of pH, and shaking time has been studied. Different kinetic and adsorption isotherm models related with the process are evaluated.

2. Materials and method

2.1. Materials

Acetonitrile (ACN, analytical reagent grade, >99.9%), divinylbenzene (DVB, analytical reagent grade, 80%), and methanol (analytical reagent grade, >99.9%) were obtained from Merck, α-α´-azobisisobutyronitrile (AIBN, purum, g 98%), glycidyl methacrylate (GMA, g 97%) was obtained from Fluka, MG (90%) was purchased from Merck. These chemical were used as such without further treatment.

2.2. Synthesis of poly GMA/DVB

Divinyl benzene (2.5 ml), 120 ml of acetonitrile (ACN), and 62.5 mg of azobisisobutyronitrile (AIBN) were taken in a round bottom flask. The mixture of all these was heated at 60˚C for 4 h and 5 ml glycidyl methacrylate (GMA) and 100 mg AIBN were also added into the mixture. It was then heated at 70˚C for 16 h with continuous stirring. Mixture was converted to white powder on cooling to room temperature. The product was filtered and washed thoroughly in a crucible with ACN and then finally with methanol. The synthesized polymer was finally dried under vacuum at room temperature for 4 h [25]. This material was stored in a desiccator and used as an adsorbent for the removal of MG. The structures of the synthesized polymer and MG are shown in Fig. 1, while the detail about the MG is given in Table 1.

2.3. Time optimization

In order to optimize shaking time, 5 ppm solution of MG was prepared in 250 ml flask in deionized water. Twenty-five milliliter of that solution was taken in 10 different titrating flasks. Optimized amount of poly GMA/DVB (0.2 g) was added in each flask. Then, all the 10 flasks were placed in the electric shaker for shaking at 120 strokes per minute. After every 10 min one of those 10 flasks was taken out, filtered, and absorbance of the filtrate was measured at 620 nm (λ_{max} of MG) by using UV/visible spectrophotometer (Analytika Jena Vario 6, Germany). The adsorption capacity of the polymer was calculated by Eq. (1).

$$q_e = \frac{C_{ad} \times A \times V}{m \times 1,000} \tag{1}$$

where q_e is the adsorption capacity (amount adsorbed per gram of the adsorbent), C_{ad} the concentration of dye adsorbed on the adsorbent, A the molecular weight of MG, V the volume of the dye solution, and m is the amount of adsorbent used for the adsorption purpose. Graph between q_e and time (Fig. 2(a)) shows that the equilibrium was attained at 50 min, so this shaking time was chosen for further studies. The collected data were used for kinetic studies.

Table 1
Detail of the dyestuff used

Dyestuff	Basic Green 4 (BG 4)
IUPAC name	4-[(4-dimethylaminophenyl)-phenyl-methyl]N,N-dimethyl-aniline
Commercial name	Malachite green (MG)
Appearance	Green crystalline powder
Molecular weight	365 g/mol
Empirical formula	$C_{23}H_{25}N_2Cl$
λ_{max}	620 nm

2.4. Concentration variations

Solutions of different concentrations of MG ranging from 0.5 to 5 ppm were prepared in deionized water. After that 25 ml of each solution was taken in titrating flask. An optimized amount (0.2 g) of polymer adsorbent was added to all the solutions. These flasks were then shaken in an electric shaker for 50 min at the rate of 120 strokes per minute. After 50 min, the solutions were filtered and the absorbance was measured at 620 nm (Fig. 2(b)). The amount of dye adsorbed q_e was calculated using Eq. (1) and this data were used in different isotherm models.

2.5. pH optimization

To study the effect of pH for adsorption of MG on poly GMA/DVB 5 ppm solution was selected. Twenty-five milliliter of each of 7 solutions with different pH (1–7) was taken in titration flask. The pH of the solution was adjusted by the addition of HCl. An amount of 0.2 g of polymer adsorbent was added to every flask and was shaken for 50 min at 120 strokes per minute, solutions were filtered, and absorbance was measured at 620 nm and finally the amount adsorbed on the surface of adsorbent was calculated using Eq. (1).

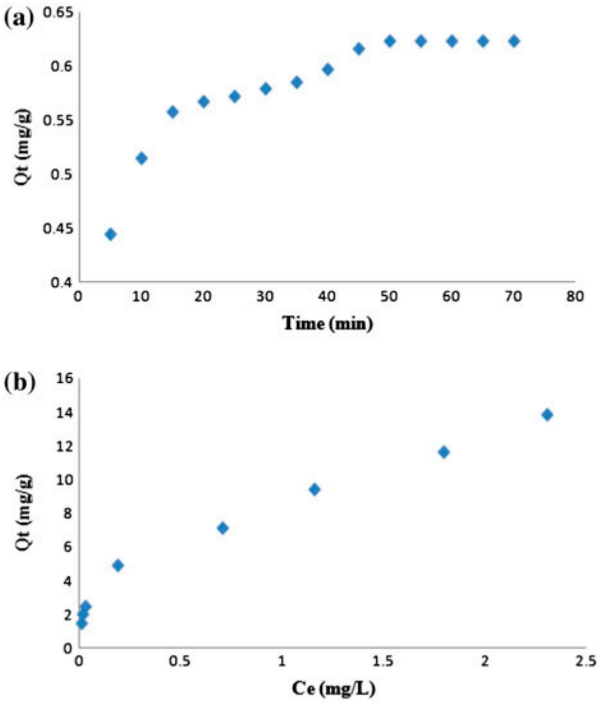

Fig. 2. (a) Graph showing the effect of shaking time and (b) effect of change in concentration on adsorption capacity of malachite green on poly GMA/DVB.

3. Results and discussion

3.1. Characterization of adsorbent

Fourier transform infrared spectroscopy (FTIR-8400 Shimadzu, Japan) analysis was also carried out for functional group analysis. The FTIR spectrum for the synthesized polymer is shown in Fig. 3. In FTIR spectrum characteristic peaks around 1,630–1,725 cm^{-1} confirm the formation of poly GMA/DVB. Peaks appearing in the range of 1,700–1,725 cm^{-1} correspond to C=O group present in poly GMA/DVB and the presence of peak at 1,637 cm^{-1} confirms the presence of C=C bond. Peaks at 2,900–3,000 cm^{-1} correspond to CH stretching of the acrylate group, while the peaks at 900–908 $\text{cm}^{-1}$are correspondent peaks of the epoxy group in GMA. A very broad IR absorption peak at 3,465 cm^{-1} represents hydroxyl group which is due to the ring opening reaction of the epoxy group in GMA. The FTIR data confirm the formation of GMA/DVB polymer.

For further investigations, quantitative analysis of the material is carried out by energy dispersive X-ray spectroscopy (EDS, JEOL JSM5800, Japan) to find out the elemental composition of the polymer adsorbent. The spectrum and the images for both before and after adsorption are shown in Fig. 4. Spectrum is recorded in the range of 0–10 keV. The presence of high intensity peak at 0.2 keV indicates carbon which is 74.06% of the total weight of the material. Another major peak appears at 0.5 keV which belongs to oxygen and is about 25.64% by weight. Atomic percentage of the carbon and oxygen is 79.29 and 20.61, respectively. High intensity peak at 0.2 keV belongs to carbon and is

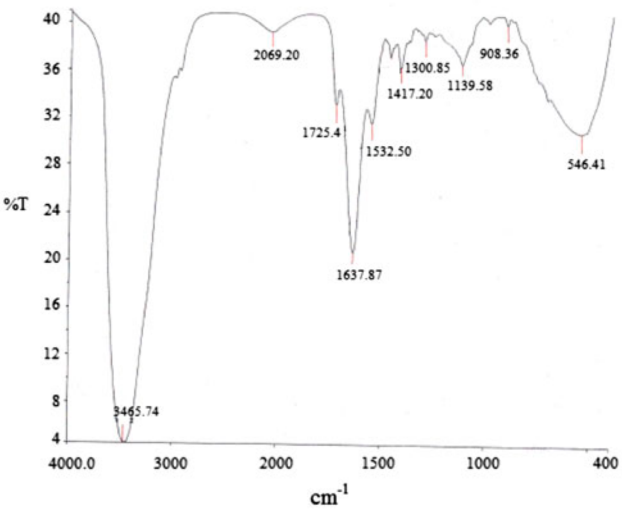

Fig. 3. FTIR spectrum of synthesized poly GMA/DVB.

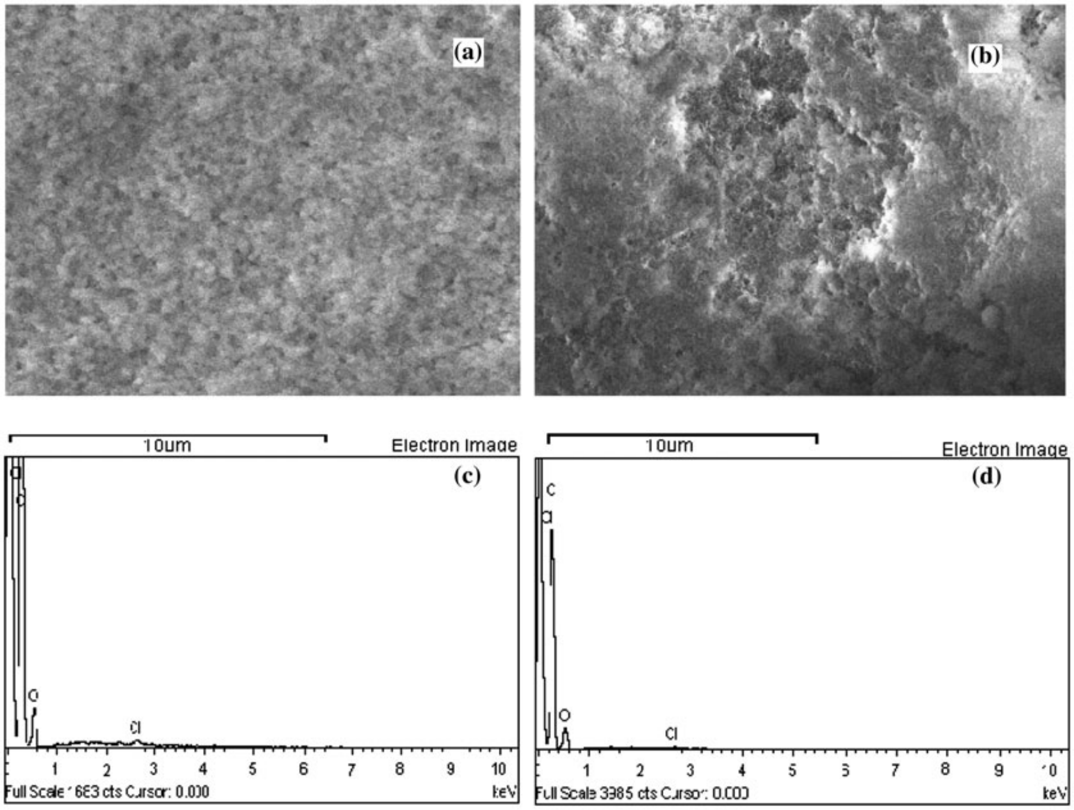

Fig. 4. EDX analysis of poly GMA/DVB (a) electron image of poly GMA/DVB before adsorption, (b) electron image of poly GMA/DVB after adsorption of malachite green, (c) figure showing elemental composition before adsorption, and (d) elemental composition of poly GMA/DVB after adsorption.

about 75.93% by weight. Oxygen peak appears at 0.5 keV and is 19.01% of the total weight of the material. Atomic percentage of the carbon and oxygen is 79.01 and 20.77, respectively. Energy dispersive X-ray spectroscopy (EDX) analysis shows that carbon and oxygen content increases after adsorption which confirms that the adsorption of MG takes place on the surface of polymeric adsorbent.

Scanning electron microscopy (SEM) analysis is another wonderful way to analyze the surface mor-

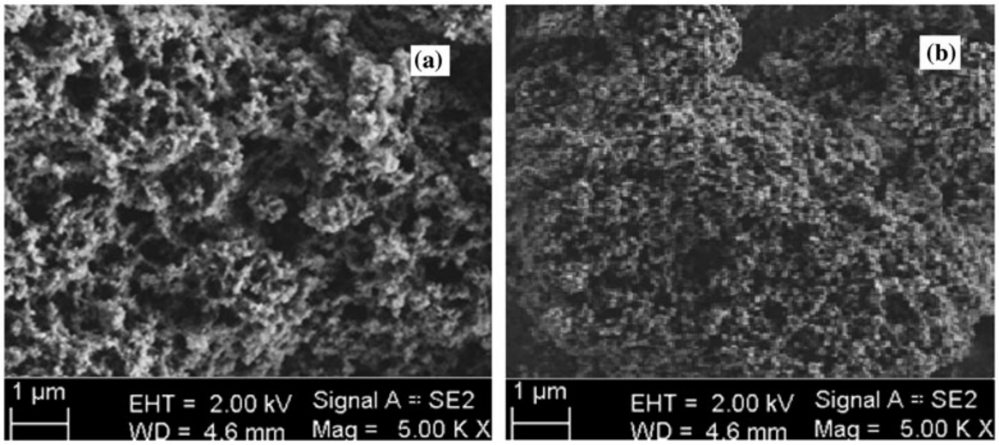

Fig. 5. SEM results of GMA/DVB (a) before adsorption (b) after adsorption.

phology of any material. Synthesized poly GMA/DVB was characterized by SEM (SEM JEOL JSM 6700F) to analyze the surface morphology. Particle size of the synthesized material is found to be in micrometer range. Fig. 5(a) shows the SEM micrograph of poly GMA/DVB before adsorption of MG. It can be seen that the surface of the polymer is porous which is beneficial for the adsorption of MG. Fig. 5(b) shows the SEM image after adsorption on the surface of polymer adsorbent. The less porosity level indicates that the adsorbate filled the pores on the surface of adsorbent.

3.2. Adsorption kinetics

It was observed that adsorption of dyes increased with increasing shaking time and attained a constant value at equilibrium after a specific time. It was observed that the uptake of dye is fast at initial stages of the contact period and thereafter, it becomes slower near the equilibrium. This is due to the fact that large numbers of vacant surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between adsorbate molecules on the solid and bulk phases. The shaking required to achieve maximum adsorption of MG on polymer adsorbent is 50 min which was used for further experiments (Fig. 2(a)).

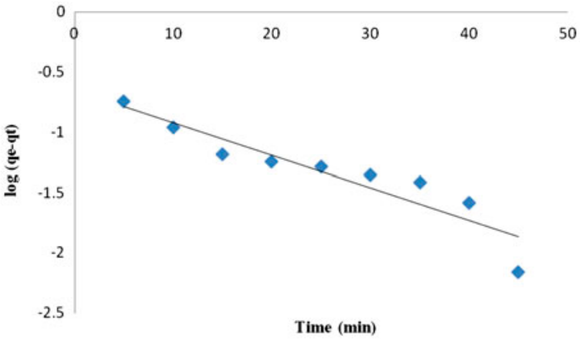

Fig. 6. Pseudo first order kinetics graph for the removal of malachite green on poly GMA/DVB.

In order to obtain rate constants, equilibrium adsorption capacity, adsorption mechanism, and determination of the rate-controlling step different kinetic models namely, pseudo-first, pseudo-second-order, and intra-particle diffusion models have been used to test the experimental data.

Pseudo-first-order equation is expressed as follows (Eq. 2) [26]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

where k_1 is the pseudo-first-order rate constant (per min), q_t the amounts of dye adsorbed at time t (min), and q_e is the amounts of dye adsorbed (mgg^{-1}) at equilibrium.

The pseudo-first-order rate constant k_1 and the equilibrium adsorption capacity q_e are determined from the slope and intercept of the plots of log $(q_e - q_t)$ vs. t (Fig. 6) and their values are given in Table 2. This kinetic data shows that the correlation coefficient for the pseudo-first kinetic model is very low (Table 2). Moreover, a large difference between theoretical and experimental equilibrium adsorption capacity q_e is also observed, which indicates that the pseudo-first equation is not fit to the experimental data. Therefore, pseudo-second model has been employed to the data.

The pseudo-second model can be represented in Eq. (3) [27]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order adsorption. The values of k_2 and the equilibrium adsorption amount (q_e) were determined from the slope and intercept of the plot of t/q_t vs. t (Fig. 7). In contrary to pseudo-first-order, the correlation coefficient (R^2) for the pseudo-second-order kinetic at different initial MG concentration is above 0.9987 and the calculated q_e values are also close to the experimental q_e. The adsorption kinetics of MG onto poly GMA/DVB has followed the pseudo-second-order kinetic model.

The intra-particle diffusion model has also been fitted to the adsorption data in order to see the

Table 2
Various kinetics parameters for the removal of malachite green using poly GMA/DVB

1st order kinetics			2nd order kinetics			Intra particle diffusion model		
q_e (±0.01)	K_1 (±0.01)	R^2	q_e (±0.01)	K_2 (±0.01)	R^2	C (±0.01)	K_{ID} (±0.01)	R^2
0.522	−0.065	0.861	0.637	0.263	0.999	0.324	0.405	0.881

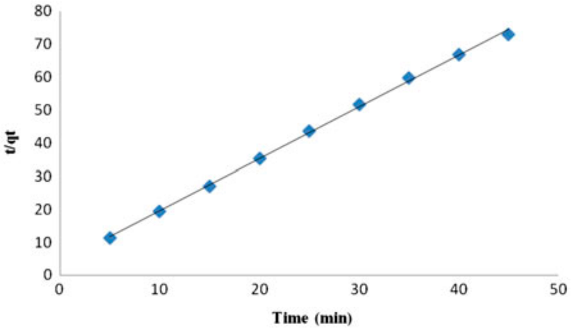

Fig. 7. Pseudo-second-order kinetics plot the adsorption of malachite green using poly GMA/DVB.

adsorption mechanism of MG. According to that model, initial rate of intra-particle diffusion can be calculated by Eq. (4):

$$q_t = K_{ID}\sqrt{t} + C \tag{4}$$

where K_{ID} (mgg^{-1} min$^{1/2}$) is the intra-particle diffusion rate constant, C is the constant, and t is contact time (min), which gives the idea on the thickness of the boundary layer. The value of C is proportional to the thickness of the boundary of the layer. The plot of q_t vs. $t^{1/2}$ (Fig. 8) gives the value of rate constants K_{ID} from the slope. The plot of q_t vs. $t^{1/2}$ should be a straight line if diffusion plays a role in the adsorption rate and if intra-particle diffusion is the rate determining step then the plot should give zero value of intercept. The slope of the initial linear portion has been used to derive the intra-particle rate constant K_{ID}. The plot of q_e vs. $t^{1/2}$ for adsorption of MG on poly GMA/DVB adsorbent shows three distinct regions. The initial linear region relates to the external surface uptake, the second stage corresponds to the gradual uptake reflecting intra-particle diffusion which may be considered as the rate-limiting step and last region indicates equilibrium uptake. So, from these results it might be concluded that intra-particle diffusion is involved in adsorption of MG onto poly GMA/DVB and adsorption process follows pseudo-second-order kinetics.

3.3. Adsorption isotherm models

The adsorption isotherms indicate how the dye molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. At an optimized time of 50 min, it was observed that adsorption capacity increases with the increase in concentration of dye solutions (Fig. 2(b)). To examine the relationship between adsorbent and adsorbate at equilibrium, and to search for the maximum sorption capacity of adsorbent, equilibrium isotherm models such as Freundlich, Langmuir, D–R, F–H, and Temkin are applied on the experimental data.

Freundlich model can be described by Eq. (5) [28]:

$$\ln q_e = K_F + \frac{1}{n}\ln C_e \tag{5}$$

where K_F (mgg^{-1}) is the Freundlich constant, related to the binding energy, can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent, and n is a heterogeneous factor which is related to the adsorption intensity of dye onto the adsorbent. In general, $n > 1$ suggests that adsorbate is favorably adsorbed on the adsorbent. The values of n and K_F are calculated from the slope and intercept of the plot ln C_e vs. ln q_e (Fig. 9), respectively, and their values are given in Table 3. The value of n is greater than 1 indicating

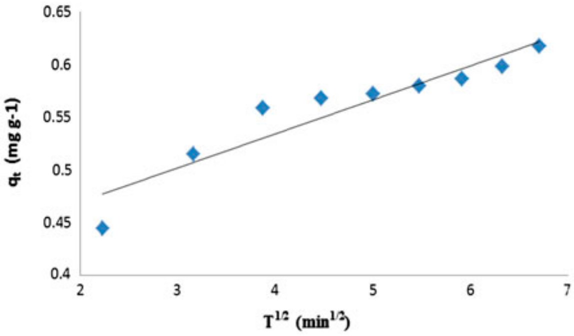

Fig. 8. Intraparticle diffusion model plot for the removal of malachite green by poly GMA/DVB.

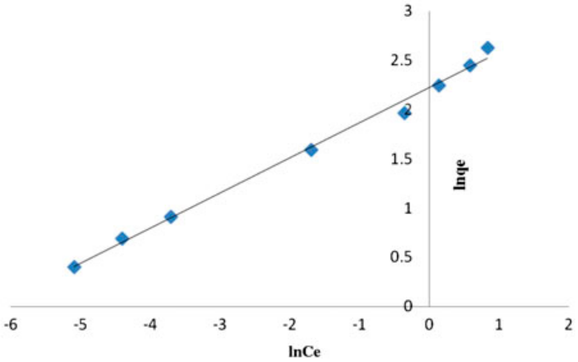

Fig. 9. Freundlich isotherm for the adsorption of malachite green on poly GMA/DVB.

Table 3
Parameters for different adsorption isotherms for removal of malachite green using poly GMA/DVB

Isotherms models	Parameters	Values
Freundlich model	n (±0.01)	2.808
	K_F (±0.1)	9.221
	R^2	0.994
Langmuir model	q_m (±0.1)	13.6
	a_L (±0.01)	4.205
	K_L (±1)	56.818
	R^2	0.935
Temkin model	K_t (±1)	196.28
	B_t (±0.01)	1.859
	R^2	0.897
Dubinin–Radushkvich model	X_m (±0.1)	9.407
	K_{DR} (±0.01)	−0.0001
	R^2	0.902
	K_{FH} (±0.01)	0.123
F–H Model	n (±0.01)	−0.602
	R^2	0.982

that the adsorption of MG is favorable onto the surface of synthesized polymer.

Langmuir equation is given as (Eq. (6)) [28]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + a_L \frac{C_e}{K_L} \tag{6}$$

where q_e and C_e correspond to the amount adsorbed per gram of adsorbent (mgg^{-1}) and equilibrium concentration (mgL^{-1}), respectively. The constants a_L and K_L are related to the adsorption capacity (mgg^{-1}) and the intensity of adsorption (mg^{-1}), respectively. A plot of C_e/q_e vs. C_e gives the values of a_L and K_L from the slope and intercept, respectively (Fig. 10). The Langmuir parameters are given in Table 3. The maximum adsorption capacity is calculated from Eq. (7):

$$q_m = \frac{K_L}{a_L} \tag{7}$$

The maximum adsorption capacity obtained from above equation is found to be 13.6 mg g^{-1}. These results are compared with the other adsorbents used for the adsorption of MG reported in the literature and their values are given in Table 4 [29–38]. It is clear from the table that most of the adsorbents showed lower adsorption capacity as compared to the present work which indicate that the polymer can be considered as a better adsorbent for the removal of MG from the aqueous media.

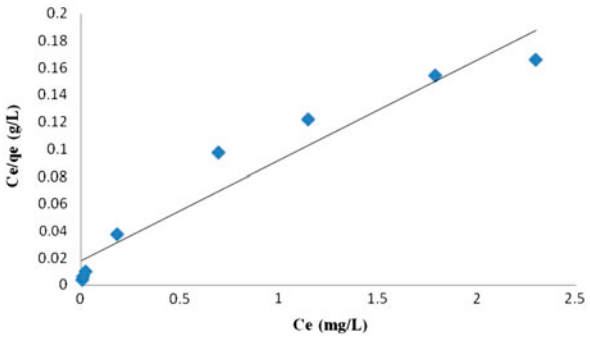

Fig. 10. Langmuir plot for the removal of malachite green using poly GMA/DVB.

Gibbs free energy (ΔG) is also calculated using Eq. (8) [39]:

$$\Delta G = -RT \ln K_L \tag{8}$$

The value of ΔG obtained from experimental data is found to be −7.46 kJ/mol. Negative value of ΔG indicates that the adsorption process is spontaneous.

Dubininan–Radushkevich (D–R) model is applied to find the mean free energy E of adsorption process. If the value of E is between 8 and 16 kJ/mol, then the adsorption process follows by chemical ion-exchange, and if $E < 8$ kJ/mol the adsorption process is of physical nature, whereas if the value is more than 16 kJ/mol, then chemisorption process take place.

Table 4
Comparison of adsorption capacity of different adsorbents used for malachite green adsorption on poly GMA/DVB

Serial No.	Adsorbents	q_m (mg/g)	Refs.
1	Arundodonax root carbon	8.90	[29]
2	Hen feather	10.3–10.7	[30]
3	Activated charcoal	0.18	[31]
4	Bentonite clay	7.72	[32]
5	Sugarcane dust	4.88	[33]
6	Activated carbon commercial grade	8.27	[34]
7	Lemon peel	3.2–51.4	[35]
8	Tamarind fruit shell	1.95	[36]
9	Cellulose	2.42	[37]
10	Ricinuscommunisepicarp based activated carbon	5.33	[01]
11	Neem sawdust	4.35	[05]
12	Rice husk	7.40	[21]
13	Polymeric gel (C4)	4.90	[38]
14	Poly(GMA/DVB) polymer	13.6	Present work

Linear form of D–R is by Eq. (9) [38]:

$$\ln q_e = \ln X_m - K_{DR}\varepsilon^2 \tag{9}$$

where K_{DR} ($\text{mol}^2\,\text{k}^{-1}\,\text{J}^{-2}$) is a constant related to the mean adsorption energy E and is the Polanyi potential, which can be calculated from Eq. (10):

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \tag{10}$$

The slope of the plot of ln q_e vs. ^{2} gives K_{DR} (mol^2/kJ^2) and the intercept shows the adsorption capacity Xm (mgg^{-1}) in (Fig. 11). The mean adsorption energy (E) can also be calculated by the following Eq. (11).

$$E = 1/\sqrt{-2}\,K_{DR} \tag{11}$$

The value of E calculated from our experimental data is 70.71 kJ mol^{-1} which indicates that the chemisorption process took place for the adsorption of MG on to the polymer adsorbent.

Flory–Huggins (F–H) isotherm was used to calculate the degree of surface coverage characteristics of the dye on the polymer adsorbent. Equation for F–H isotherm is given in Eq. (12) [40]:

$$\ln Q/C = \ln K_{FH} + n\,\ln(1-Q) \tag{12}$$

where $Q = (1 - C_e/C)$ is the degree of surface coverage, n is the number of MG molecule as occupying adsorption sites of the polymer adsorbent, and K_{FH} is the equilibrium constant. The values of n and K_{FH} are calculated from the slope and intercept of the plot between log Q/C vs. ln $(1 - Q)$ (Fig. 12). The value of K_{FH} and n from graph are calculated which are 0.1234 and −0.6023, while the value of R^2 is 0.9817 which are listed in (Table 3). These results indicate that MG is adsorbed on the surface of the poly GMA/DVB.

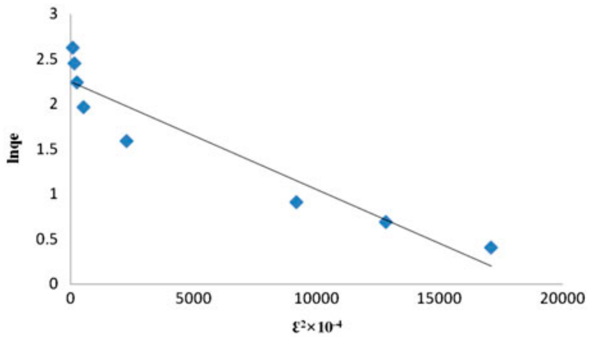

Fig. 11. D–R Isotherm for the adsorption of malachite green on poly GMA/DVB.

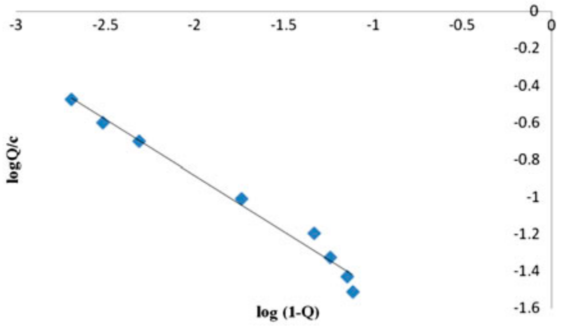

Fig. 12. F–H Model plot for the adsorption of malachite green on poly GMA/DVB.

The Gibbs free energy can also be calculated from the value of K_{FH} as follows (Eq. 13):

$$\Delta G = -2.303\,RT\ln K_{FH} \tag{13}$$

where T is the absolute temperature (K) and R is the universal gas constant (R = 8.3143 Jmol^{-1} K^{-1}). The value of ΔG obtained is −5.71 kJmol^{-1}, negative values of ΔG confirmed that the adsorption process is spontaneous process.

Temkin isotherm is also applied to further analyze the data. This model suggests that heat of adsorption of every molecule in the layer shows linear decreases due to interaction between adsorbate and adsorbent interactions.

The linear form of this Temkin model is given as Eq. (14) [41]:

$$Q_e = \beta_t\ln K_t + \beta_t\ln C_e \tag{14}$$

where K_t is the equilibrium binding constant or Temkin adsorption potential constant and it corresponds to the maximum binding energy, whereas B_t is given by Eq. (15).

$$B_t = R_t/b \tag{15}$$

It is related to the heat of adsorption [42]. The values of K_t and B_t obtained from the intercepts and slopes of the plots of q_e vs. ln C_e, respectively (Fig. 13). In Temkin isotherm, there is a factor takes in to account the interactions between adsorbate and adsorbent. The value of Temkin adsorption potential constant K_t is calculated and is found to be196.282/mg at temperature 310 K for adsorption MG. The value of Temkin constant B_t calculated 1.8587 that is related to the heat

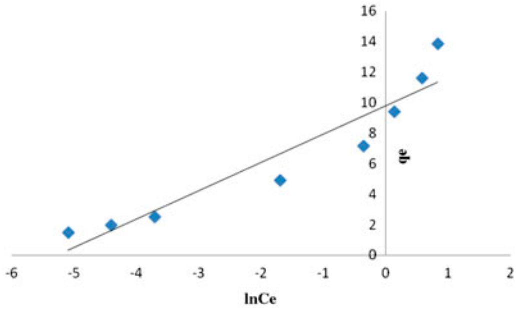

Fig. 13. Temkin model graph for the removal of malachite green using poly GMA/DVB.

of MG adsorption onto poly GMA/DVB confirming a strong interaction between MG ions and the adsorbents surface. From this chemisorption mechanism for the MG adsorption process is also evident.

3.4. Effect of pH

pH is considered to be one of the most important parameters which effect the adsorption mechanism. Effect of pH on adsorption process is due to the fact that it affects surface charge of adsorbent, speciation of the adsorbate, and the degree of ionization which is related to a competition of hydrogen ion and adsorbate ions on the active sites of the adsorbent material. The effect of pH on adsorption of MG on poly GMA/DVB is evaluated in the pH range of 7 (Fig. 14), because after pH 7 the color of the dye changes. The adsorption of MG on the polymeric surface increases with the increase in pH. At lower pH value the H$^+$ ions adsorbed on the surface of adsorbent and the surface of the adsorbent become positively charged. The dye has also positive charge so there is repulsion between positively charged surface of the adsorbent and adsorbate. As the value of pH increases, the H$^+$ ion decreases on the surface and as a result the adsorption of MG increases with the increase in pH.

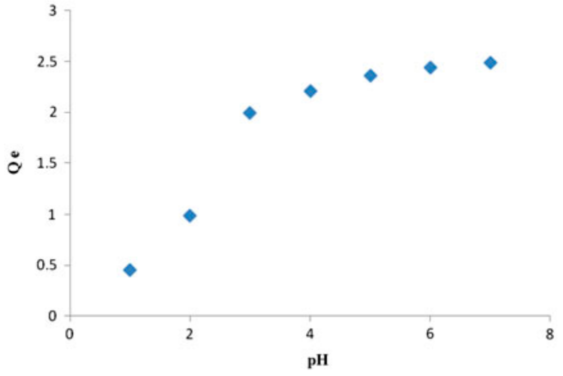

Fig. 14. Graph showing the effect pH on adsorption capacity of malachite green on poly GMA/DVB.

4. Conclusion

The present study shows that poly GMA/DVB polymer has been synthesized successfully which is confirmed by the FTIR studies. The SEM confirms that there are pores on the surface of polymer which are beneficial for the adsorption process. Kinetics studies show that the adsorption process follows the pseudo-second-order kinetic model, while the intra-particles diffusion model shows that the adsorption process takes place in three steps. The negative value of thermodynamic parameter ΔG showed that the adsorption process for dye on the adsorbent is spontaneous. The values of binding energy and Temkin constant (B_t) indicates that the adsorption of MG is chemisorptions. Effect of shaking time, initial dye concentration, and pH was also studied and it was concluded that this polymer adsorbent works efficiently at neutral pH. The adsorption capacity (13.6 mg g^{-1}) of the investigated adsorbent is higher than that of others reported in the literature. Therefore, it can be a good alternate and promising material for the removal of MG from aqueous medium.

References

[1] T. Santhi, S. Manonmani, T. Smitha, Removal of malachite green from aqueous solution by activated carbon prepared from the epicarp of Ricinuscommunis by adsorption, J. Hazard. Mater. 179 (2010) 178–186.

[2] R. Jain, V.K. Gupta, S. Sikarwar, Adsorption and desorption studies on hazardous dye Naphthol Yellow S, J. Hazard. Mater. 182 (2010) 749–756.

[3] S. Nethaji, A. Sivasamy, G. Thennarasu, S. Saravanan, Adsorption of Malachite Green dye onto activated carbon derived from *Borassusaethiopum* flower biomass, J. Hazard. Mater. 181 (2010) 271–280.

[4] A. Mittal, V. Thakur, V. Gajbe, Adsorptive removal of toxic azo dye Amido Black 10B by hen feather, Environ. Sci. Pollut. Res. 20 (2013) s260–s269.

[5] S.D. Khattri, M.K. Singh, Removal of malachite green from dye wastewater using neem sawdust by adsorption, J. Hazard. Mater. 167 (2009) 1089–1094.

[6] R. Jain, P. Sharma, S. Sikarwar, Kinetics and isotherm analysis of Tropaeoline 000 adsorption onto unsaturated polyester resin (UPR): A non-carbon adsorbent, Environ. Sci. Pollut. Res. 20 (2013) 1493–1502.

[7] A. Mittal, D. Jhare, J. Mittal, Adsorption of hazardous dye Eosin Yellow from aqueous solution onto waste material De-oiled Soya: Isotherm, kinetics and bulk removal. J. Mol. Liq. 179 (2013) 133–140.

[8] V.K. Gupta, A. Mittal, D. Jhare, J. Mittal, Batch and bulk removal of hazardous colouring agent Rose Bengal by adsorption techniques using bottom ash as adsorbent, RSC Adv. 2 (2012) 8381–8389.

[9] P. Saha, S. Chowdhury, S. Gupta, I. Kumar, Insight into adsorption equilibrium, kinetics and thermodynamics of Malachite Green onto clayey soil of Indian origin, Chem. Eng. J. 165 (2010) 874–882.

[10] L.D. Fiorentin, D.E.G. Trigueros, A.N. Modenes, F.R. Espinoz-Quinones, N.C. Pereira, S.T.D. Barros, O.A.A. Santos, Biosorption of reactive blue 5G dye onto Drying orange bagasse in batch system: Kinetic and equilibrium modeling, Chem. Eng. J. 163 (2010) 68–77.

[11] H.B. Senturk, D. Ozdes, C. Duran, Biosorption of Rhodamine 6G from aqueous solutions onto almond shell (Prunusdulcis) as a low cost biosorbent, Desalination 252 (2010) 81–87.

[12] R. Ahmad, R. Kumar, Adsorption studies of hazardous malachite green onto treated ginger waste, J. Environ. Manage. 91 (2010) 1032–1038.

[13] J. Chen, J. Mao, X. Mo, J. Hang, M. Yang, Study of adsorption behavior of malachite green on polyethylene glycol micelles in cloud point extraction procedure, Colloids and Surfaces A: Physicochem, Eng. Aspects 345 (2009) 231–236.

[14] S.J. Culp, J.R. Blankenship, D.F. Kusewitt, D.R. Doerge, L.T. Mulligan, F.A. Beland, Toxicity and metabolism of malachite green and leuco malachite green during short-term feeding to Fischer 344 rats and $B_6C_3F_1$ mice, Chem-Biol. Interact. 122 (1999) 153–170.

[15] S.J. Culp, F.A. Beland, Malachite green: A toxicological review, J. Am. Coll. Toxicol. 15 (1996) 219–238.

[16] K.V.K. Rao, Inhibition of DNA synthesis in primary rat hepatocyte cultures by malachite green: A new liver tumor promoter, Toxicol. Lett. 81 (1995) 107–113.

[17] S. Srivastava, R. Sinha, D. Roy, Toxicological effects of malachite green, Aquat. Toxicol. 66 (2004) 319–329.

[18] S. Chowdhury, P. Saha, Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: Equilibrium, kinetic and thermodynamic studies, Chem. Eng. J. 164 (2010) 168–177.

[19] R. Han, Y. Wang, Q. Sun, L. Wang, J. Song, X. He, C. Dou, Malachite green adsorption onto natural zeolite and reuse by microwave irradiation, J. Hazard. Mater. 175 (2010) 1056–1061.

[20] S. Chowdhury, R. Mishra, P. Saha, P. Kushwaha, Adsorption thermodynamics, kinetics and iso-steric heat of adsorption of malachite green onto chemically modified rice husk, Desalination 265 (2011) 159–168.

[21] B. Samiey, A.R. Toosi, Adsorption of malachite green on silica gel: Effects of NaCl, pH and 2-propanol, J. Hazard. Mater. 184 (2010) 739–745.

[22] Y. Kismir, A.Z. Aroguz, Adsorption characteristics of the hazardous dye Brilliant Green on Saklıkent mud, Chem. Eng. J. 172 (2011) 199–206.

[23] B.H. Hameed, M.I. El-Khaiary, Malachite green adsorption by rattan sawdust: Isotherm, kinetic and mechanism modeling, J. Hazard. Mater. 159 (2008) 574–579.

[24] H. Zhang, Y. Tang, X. Liu, Z. Ke, X. Su, D. Cai, X. Wang, Y. Liu, Q. Huang, Z. Yu, Improved adsorptive capacity of pine wood decayed by fungi Poriacocos for removal of malachite green from aqueous solutions, Desalination 274 (2011) 97–104.

[25] J.M. Jin, J.M. Lee, M.H. Ha, K. Lee, S. Choe, Highly crosslinked poly (glycidylmethacrylate-co-divinyl benzene) particles by precipitation polymerization, Polymer 48 (2007) 3107–3115.

[26] S. Lagergren, About the theory of so-called adsorption of soluble substances, K. Sven. Vetenskapsakad. Handl. 24 (1998) 1–39.

[27] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (2000) 735–742.

[28] E. Bulut, M. Ozacar, Adsorption of malachite green onto bentonite: Equilibrium and kinetic study and process design, Microporous Mesoporous Mater. 115 (2008) 234–246.

[29] J. Zhang, Y. Li, C. Zhang, Y. Jing, Adsorption of malachite green from aqueous solution onto carbon prepared from *Arundodonax* root, J. Hazard. Mater. 150 (2008) 774–782.

[30] A. Mittal, Adsorption kinetics of removal of a toxic dye, Malachite Green, from wastewater by using hen feathers, J. Hazard. Mater. 133 (2006) 196–202.

[31] M.J. Iqbal, M.N. Ashiq, Adsorption of dyes from aqueous solutions on activated charcoal, J. Hazard. Mater. 139 (2007) 57–66.

[32] S.S. Tahir, N. Rauf, Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay, Chemosphere 63 (2006) 1842–1848.

[33] S.D. Khattri, M.K. Singh, Colour removal from dye waste water using sugarcane dust as an adsorbent, Adsorpt. Sci. Technol. 17 (1999) 269–282.

[34] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses, Colloids Surf. A 264 (2005) 17–28.

[35] K. Kumar Vasanth, Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel, Dyes Pigm. 74 (2007) 595–597.

[36] P. Saha, S. Chowdhury, S. Gupta, I. Kumar, R. Kumar, Assessment on the removal of malachite green using tamarind fruit shell as biosorbent, Clean: Soil Air Water 38 (2010) 437–445.

[37] C.P. Sekhar, S. Kalidhasan, V. Rajesh, N. Rajesh, Bio-polymer adsorbent for the removal of malachite green from aqueous solution, Chemosphere 77 (2009) 842–847.

[38] M.A. Malana, S. Ijaz, M.N. Ashiq, Removal of various dyes from aqueous media onto polymeric gels by adsorption process: Their kinetics and thermodynamics, Desalination 263 (2010) 249–257.

[39] G.H. Sonawane, V.S. Shrivastava, Kinetics of decolourization of malachite green from aqueous medium by maize cob (*Zea maize*): An agricultural solid waste, Desalination 247 (2009) 430–441.

[40] K.R. Ramakrishna, T. Viraraghvan, Dye removal using low cost adsorbents, Water Sci. Technol. 36 (1997) 189–196.

[41] S. Tuba, Removal of some fungicides from aqueous solution by the biopolymer chitin, Colloids Surf., A 297 (2007) 38–45.

[42] M.H. Jnr, A.I. Spiff, Equilibrium sorption study of Al^{3+}, Co^{2+} and Ag^{+} in aqueous solution by fluted pumpkin (telfairiaoccidentalis HOOK) waste biomass, Acta Chem. Slov. 52 (2005) 174–181.