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Efficient removal of malachite green dye using biodegradable graft copolymer derived from amylopectin and poly(acrylic acid)

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ABSTRACT

This article reports on the application of a high performance biodegradable adsorbent based on amylopectin and poly(acrylic acid) (AP-g-PAA) for removal of toxic malachite green dye (MG) from aqueous solution. The graft copolymer has been synthesized and characterized using various techniques including FTIR, GPC, SEM and XRD analyses. Biodegradation study suggests that the co-polymer is biodegradable in nature. The adsorbent shows excellent potential (Q_{max}, 352.11 mg g^{-1}; 99.05% of MG has been removed within 30 min) for removal of MG from aqueous solution. It has been observed that point to zero charge (*pzc*) of graft copolymer plays significant role in adsorption efficacy. The adsorption kinetics and isotherm follow pseudo-second order and Langmuir isotherm models, respectively. Thermodynamics parameters suggest that the process of dye uptake is spontaneous. Finally desorption study shows excellent regeneration efficiency of adsorbent.

1. Introduction

One of the major sources of water pollution is colored wastewater, which is coming out from dye, pigment as well as from textile industries. The increase in population also increases the requirement of millions of tons of dyes, those are being consumed by various textile industries (Gupta & Suhas, 2009). Because of the complex structure of basic dyes and toxic nature of their degraded products, they are being considered as non-biodegradable. It has been reported that even less than 1 ppm of dye makes the industrial effluent colored (Mohan, Singh, Singh, & Kumar, 2002). The colored wastewater is a real threat to inhibit the growth of biota, enhanced the microtoxicity to aquatic life, reduced light penetration and retards photosynthetic activity (Malik, Ramteke, & Wate, 2007). Thus it is essential to decolourize the dying effluent, without disturbing the quality of water to make it reusable for various industrial and agricultural applications.

A variety of traditional methods have been employed for removal of color from dye industry effluent/wastewater, which includes coagulation/flocculation, membrane filtration, biodegradation, softening, photodegradation, oxidation and so on. The coagulation/flocculation process is effective only with insoluble dyes. The oxidation process is efficient but the requirement of oxidant is very high, which makes the process expensive. In case of biological treatment, it works well with the removal of COD and BOD but this process is having major limitation as it cannot remove color from wastewater comprehensively. Similarly, photochemical degradation in aqueous solution is likely to progress slowly and also in principle, the synthetic dyes exhibit high stability to light (Mohan et al., 2002). Thus the above mentioned processes are having certain limitations, including incomplete removal, generation of degraded products and so on. Out of various processes, liquid phase adsorption has received great interest because of its reliability and low cost in application, having high potential for discharging color and removal of organic and inorganic pollutants (Singh, Sharma, Tripathi, & Sanghi, 2009). Various adsorbents have already been reported for removal of toxic dyes, including spent rice biomass (Rehman, Kim, & Han, 2012), activated carbon (Sharma, 2011), peach gum (Zhou, Huang, He, Zhang, & Li, 2014), ginger waste (Ahmad & Kumar, 2010), rice husks (Chowdhury, Mishra, Saha, & Kushwaha, 2011), almond shell (Duran, Ozdes, Gundogdu, & Senturk, 2011) and so on. In recent years, natural polymers are used as adsorbents for removal of toxic dyes (Rahchamani, Mousavi, & Behzad, 2011; Sekhar, Kalidhasan, Rajesh, & Rajesh, 2009). In order to improve the efficiency of the adsorbent, recently various modified natural polymers have been developed and used for removal of toxic dyes from aqueous solution (Crini, Peindy, Gimbert, & Robert,

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2007; Kono, Onishi, & Nakamura, 2013; Lazaridis, Kyzas, Vassiliou, & Bikiaris, 2007).

Malachite green (MG) is a water soluble synthetic basic dye, has been used for dyeing of textile industries (Kumar, Sivanesan, & Ramamurthi, 2005). It is used in medical disinfectant and aquaculture. However, MG has become one of the most controversial dyes, because of its toxic effect (Crini et al., 2007; Srivastava, Sinha, & Roy, 2004). It has also been reported that the discharge of MG dye in water can cause severe environmental degradation as it provides undesirable color to water bodies and reduced sunlight penetration (Arellano-Cárdenas, López-Cortez, Cornejo-Mazón, & Mares-Gutiérrez, 2013; Ahmad & Kumar, 2010; Srivastava et al., 2004). Thus, it is essential to remove MG from the effluents before its discharge to water bodies. Many adsorbents have already been reported for removal of MG from aqueous effluent, like treated ginger waste (Ahmad & Kumar, 2010), rice husk (Chowdhury et al., 2011), activated carbon (Sharma, 2011), biopolymer – cellulose (Sekhar et al., 2009), polyacrylic acid-nanoclay nanocomposite (Sonawane et al., 2009), cyclodextrin (Crini et al., 2007), organically modified clay (Arellano-Cárdenas et al., 2013), polyacrylic acid-silica composite (Xu, Jia, Zhang, & Li, 2012). But still it is essential to develop new adsorbents for separation of MG from aqueous solution, for the significant shortcomings of reported adsorbents like biodegradability, higher equilibrium time and lower adsorption capacity. For example, Xu et al. (2012) reported the sorption of MG using vinyl-modified mesoporous poly(acrylic acid)/SiO_2 composite, which showed adsorption capacity of 220.49 mg g^{-1} and also 98.8% dye was removed after 240 min, Sonawane et al. (2009) used polyacrylic acid-nanoclay nanocomposite as adsorbent in sonosorption studies of MG dye having monolayer adsorption capacity of 243.11 mg g^{-1}. In view of effective removal of toxic MG, a high performance biodegradable natural polymer based adsorbent has been developed in the authors' laboratory by grafting synthetic poly(acrylic acid) chains on amylopectine backbone (Sarkar, Mandre, Panda, & Pal, 2013). It functions as an efficient adsorbent to remove toxic MG very rapidly and efficiently from aqueous solution. In addition to providing insight into the thermodynamic and kinetic aspects on adsorption, this article represents the first report on AP-g-PAA based adsorbent for uptake of MG from aqueous solution.

2. Experimental

2.1. Materials

AP-g-PAA was used as adsorbent which was synthesized before in authors' laboratory (Sarkar et al., 2013). MG (i.e. N-[4-[[4-(dimethylamino) phenyl] phynylmethylene]-2,5-cyclohexadien-1-ylidene]-N-methyl-oxalate, experimental λ_{max} of MG is 615 nm) was purchased from Loba Chemicals, India. For all the experiments, double distilled water was used.

2.2. Preparation of AP-g-PAA

The graft copolymer of amylopectin and poly(acrylic acid) (AP-g-PAA) was synthesized in a 250 mL RB flask, at a temperature of 65 °C in inert atmosphere of nitrogen. Potassium persulphate was used as an initiator. The detailed reaction procedure and conditions have been reported previously (Sarkar et al., 2013).

2.3. Characterization

FTIR spectra were recorded on a Perkin Elmer FTIR spectrometer (Model Spectrum 2000; using KBr pellet method). Gel permeation chromatography (GPC) analyses were carried out at a column temperature of 30 °C (with a flow rate of 0.6 mL/min) using a GPC system (model: 2414; Make: Waters (I) Pvt. Ltd., USA). XRD analysis was done using powder XRD (Bruker X-ray diffractometer, D8-Fecus, Germany). The surface morphology was analyzed using scanning electron microscopy (Model: S-3400N; Hitachi, Japan).

2.4. Biodegradation study

The biodegradation of AP-g-PAA film was carried out by inoculating with *Aspergillus niger* fungus. The degradation study was carried out in the similar way as reported before (Vijan, Kaity, Biswas, Isaac, & Ghosh, 2012).

2.5. Batch adsorption studies

The MG adsorption using AP-g-PAA was carried out using thermostated orbital shaker (Rivotek, Kolkata, India). The adsorption experiment was performed in similar way as reported before except centrifugation at 3000 rpm for 6 min to remove adsorbent particles (Ghorai, Sarkar, Panda, & Pal, 2013). The % of MG adsorption was calculated using Eq. (1):

$$\%\text{Adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

and the equilibrium uptake was calculated using Eq. (2)

$$q_e = (C_0 - C_e) \times \frac{V}{W} \quad (2)$$

where q_e is the equilibrium capacity of dye on the adsorbent (mg g^{-1}), C_0 is the initial concentration of dye solution (mg L^{-1}), C_e is the equilibrium concentration of dye solution (mg L^{-1}), V is the volume of dye solution used (L) and W is the weight of adsorbent (g) used (Ghorai et al., 2013).

2.6. Desorption experiments

The regeneration characteristics of AP-g-PAA 5 was investigated in four successive adsorption–desorption cycles. The details of desorption procedure have been discussed in Supporting Information.

3. Results and discussion

3.1. Synthesis

The free radical polymerization technique was carried out to synthesize AP-g-PAA, using potassium persulphate (KPS) as initiator (Sarkar et al., 2013). A probable mechanism for formation of the graft copolymer is explained in details in our earlier report (Sarkar et al., 2013). The proposed structure of AP-g-PAA is shown in Fig. S1, Supporting Information.

With variation of reaction parameters, different grades of graft copolymers have been synthesized (Table S1, Supporting Information) and the optimized one (AP-g-PAA 5) was considered with respect to its higher intrinsic viscosity, hydrodynamic radius and better rheological characteristics (Sarkar et al., 2013).

3.2. Characterization

3.2.1. FTIR

FTIR spectrum of amylopectin (Fig. 1a) shows a broad peak at 3405 cm^{-1}, which is due to the stretching frequency of —OH groups. The band at 2938 cm^{-1} is attributed to C—H stretching vibrations and 931 cm^{-1} for the C—H bending vibrations. The bands at 1081 cm^{-1} and 1021 cm^{-1} are responsible for C—O—C stretching vibrations. Bands due to —CH_2 stretching and —CH_2 bending vibrations have been observed at 1427 cm $^{-1}$ and 1248 cm^{-1},

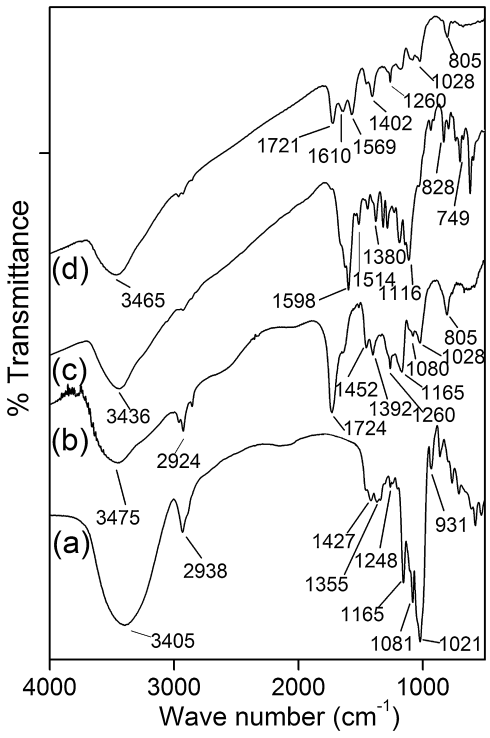

Fig. 1. FTIR spectra of (a) amylopectin, (b) AP-g-PAA 5, (c) MG and (d) MG adsorbed AP-g-PAA 5.

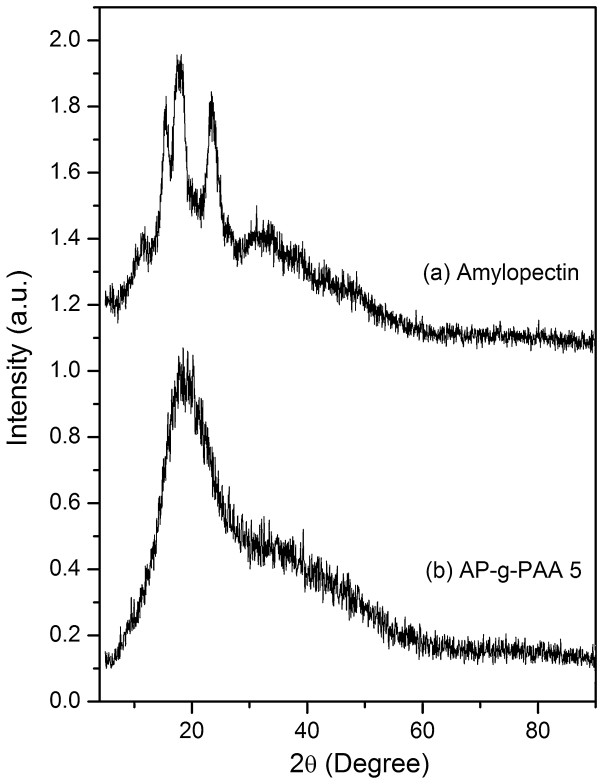

Fig. 2. X-ray difractogram of (a) amylopectin and (b) AP-g-PAA 5.

respectively (Sun, Sun, Sun, & Su, 2004). The band at 1355 cm^{-1} is because of the —OH bending vibration (Sun et al., 2004). Compared to amylopectin, AP-g-PAA 5 (Fig. 1b) has certain extra peaks. The bands at 1724 cm^{-1} and 1452 cm^{-1} are attributed to the carbonyl absorption and COO^- symmetric stretching vibrations respectively. Also the sharp peak at 805 cm^{-1} reveals that PAA has been grafted onto amylopectin (Lazaridis et al., 2007). The presence of these additional peaks suggest the successful grafting of poly(acrylic acid) on amylopectin.

3.2.2. Determination of molecular weight and molecular weight distribution using gel permeation chromatography

The results of molecular weight and molecular weight distribution of amylopectin and AP-g-PAAs are reported in Table S1, Supporting Information. It is obvious that all graft copolymers are having higher molecular weight than that of amylopectin. This is due to the presence of grafted poly(acrylic acid) chains on polysaccharide backbone. Further, AP-g-PAA 5, which is having the highest % GE, has maximum molecular weight (Table S1, Supporting Information as well as Fig. S2, Supporting Information). This indicates the presence of longer grafted chains (i.e. PAA) in this composition as higher is the % GE, longer would be the grafted chains.

3.2.3. XRD analysis

Fig. 2 shows the X-ray diffractograms of amylopectin and AP-g-PAA 5. Fig. 2a suggests that amylopectin exhibits a very small crystallinity (the peaks observed at $2\theta = 15^\circ$, 18°, 23° and 33°). It has been reported that pure poly(acrylic acid) has single diffraction peak at $2\theta = 23^\circ$ (Xu et al., 2012), confirming its amorphous structure. The graft copolymer (Fig. 2b) exhibits one broad peak at $2\theta = 19^\circ$, where as the other crystalline peaks of amylopectin disappeared. The absence of the crystalline peaks in the case of AP-g-PAA 5 (Fig. 2b) may be because of the disruption of crystalline structure by the presence of grafted poly(acrylic acid) chains.

3.3. Biodegradation study

Fig. S3, Supporting Information demonstrates the fungal growth on the surface of AP-g-PAA 5 film for 0 and 21 days. Initially (0 day) no growth was observed. However, it is obvious that fungi growth took place for 21 days in the film. The growth of fungi in mineral salts agar medium (no carbon content) confirms that the carbon present in the graft copolymer has been exploited by the fungi for its growth (Vijan et al., 2012). This confirmed the biodegradable nature of the graft copolymer.

3.4. Adsorption characteristics

The efficacy of MG adsorption from aqueous solution using AP-g-PAA depends on various factors like pH, temperature of the solution, equilibrium time of adsorption, initial concentration of the dye, the amount of adsorbent dosage, and ionic strength.

In adsorption process, particularly the uptake of dye depends highly on solution pH. To determine the optimize pH condition, the adsorption was carried out using 400 mg L^{-1} of MG to 50 mg of adsorbent. Besides, point to zero charge (*pzc*) of an adsorbent is very imperative in order to realize the effect of pH on adsorption (Wang, Zhang, & Wang, 2011). It is familiar that adsorption of a cation is favorable at pH > *pzc*, while for an anion the adsorption predominates at pH < *pzc*. It is obvious from Fig. 3a that the *pzc* of adsorbent (AP-g-PAA 5) is 5.51. It has also been observed from Fig. 3b that increase in color removal was obvious by increasing pH from 4 to 8 and after which it was in equilibrium. This is due to the fact that at higher pH, the —COOH groups present in the grafted PAA chains would dissociate to form COO^- groups, which will increase the number of ionized groups and generates the electrostatic repulsion forces among the adjacent ionized groups (Wang et al., 2011). This would expand the polymer network, which results in an increase in adsorption of MG. Besides at higher pH, the electrostatic attraction between negatively charged surface of adsorbent

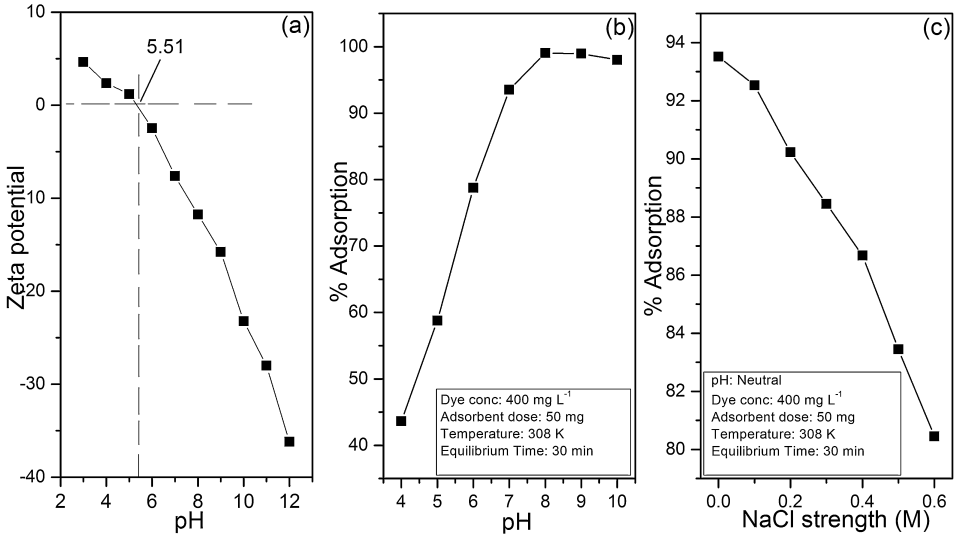

Fig. 3. (a) Effect of pH on zeta potential of AP-g-PAA 5, (b) effect of pH and (c) effect of ionic strength on % adsorption of MG using AP-g-PAA 5.

and positively charged adsorbate is enhanced, resulting higher % of adsorption.

At pH < *pzc* of adsorbent, the electrostatic repulsion between the positively charged surface of adsorbent and positively charged MG increased, which results lower % of adsorption. The similar trend of pH was observed for removal of MG using cyclodextrin based adsorbent (Crini et al., 2007).

In the textile industry, salts are extensively used for the dyeing process and it is thus essential to find out the effect of ionic strength on adsorption. Here we have varied the NaCl concentration from 0.1 to 0.6 M to determine the salt effect on MG adsorption, by keeping other parameters constant (temperature – 308 K contact time – 30 min, dye concentration – 400 mg L^{-1}, adsorbent dosage – 50 mg, pH – 7). Results (Fig. 3c) indicate that with an increase in salt concentration, adsorption efficiency gradually decreased. This is due to the fact that with increase in ionic strength, the inter ionic competition between Na^+ and cationic MG with the negatively charged surface of the adsorbent enhanced (Kuo, Wu, & Wu, 2008). This observation clearly suggests that electrostatic force of attraction is predominating between the adsorbent and the adsorbate.

The effect of temperature, contact time, dye concentration and adsorbent dosage on % of MG adsorption have been discussed in details in Supporting Information and the results are represented in Fig. S4, Supporting Information.

3.4.1. Kinetics study

The adsorption efficiency depends well on contact time of solid–liquid interface as well as diffusion process. Various kinetics models including Legergren pseudo-first order (Legergren, 1898), pseudo-second order (Ho & McKay, 1999), second order (Ho, 2006) and intraparticle diffusion (Weber & Morris, 1963) were used to assess the mechanism of adsorption (Fig. 4). The details of various models have been explained in Supporting Information.

It is obvious from the results that pseudo-second order model (Fig. 4b) exhibits higher correlation coefficient and lower χ^2 value (Table S2, Supporting Information), compared to other models. This indicates that the adsorption kinetic process follows pseudo-second order model. Further, the plot of the q_t vs. $t^{1/2}$ (Fig. 4d) is the combination of two straight lines which intersect with each other, suggesting more than one steps may control the adsorption process. The first linear segment follows a boundary layer diffusion due to surface adsorption and the second linear portion confirms the intraparticle diffusion, which plays a role in controlling the rate of adsorption (Crini et al., 2007). Besides, it has been pointed out that if the plot of q_t vs. $t^{1/2}$ is passed through the origin, then intraparticle diffusion is the rate limiting step (Ozcan & Ozcan, 2005). However, it has been observed that the plots have an intercept value (Table S2, Supporting Information), which indicates about the thickness of the boundary layer. Thus it is believed that surface adsorption as well as intraparticle diffusion may occur simultaneously for this system.

3.4.2. Adsorption isotherm

In order to investigate the interactive behavior between the adsorbent and adsorbate molecules, Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906) and Temkin (Temkin & Pyzhev, 1940) isotherm models have been studied and the results are shown in Fig. 5. The various isotherm models have been explained in details in Supporting Information.

One important parameter, known as separation factor (R_L), is an essential characteristics of the Langmuir isotherm model (Ayad & El-Nasr, 2010). This is defined by:

$$R_L = \frac{1}{1 + b \cdot C_0} \tag{3}$$

where b is the Langmuir constant and C_0 is the initial concentration of MG. The value of R_L suggests whether the Langmuir isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), irreversible ($R_L = 0$) or favorable ($0 < R_L < 1$) (Ayad & El-Nasr, 2010).

Fig. 5 demonstrates that Langmuir isotherm model is a better mathematical fit to experimental data in compared to Freundlich and Temkin isotherm models at various temperatures. It has also been observed that Langmuir isotherm model shows higher correlation coefficient and lower χ^2 value (Table S3, Supporting Information). The Langmuir constant 'b' increased with temperature, signifying the stronger attraction between the active sites of adsorbent and adsorbate. The values of R_L have been found to be less than 1 (at 308 K temperature and 400 mg L^{-1} dye concentration), which suggest the favorable uptake of MG. From Langmuir isotherm at 308 K, monolayer adsorption capacity (q_m) has been found to be 352.11 mg g^{-1}, which is considerably higher. The values of Freundlich isotherm constant (n_F) are in the range of 1–10. This supports the feasibility of the adsorption process.

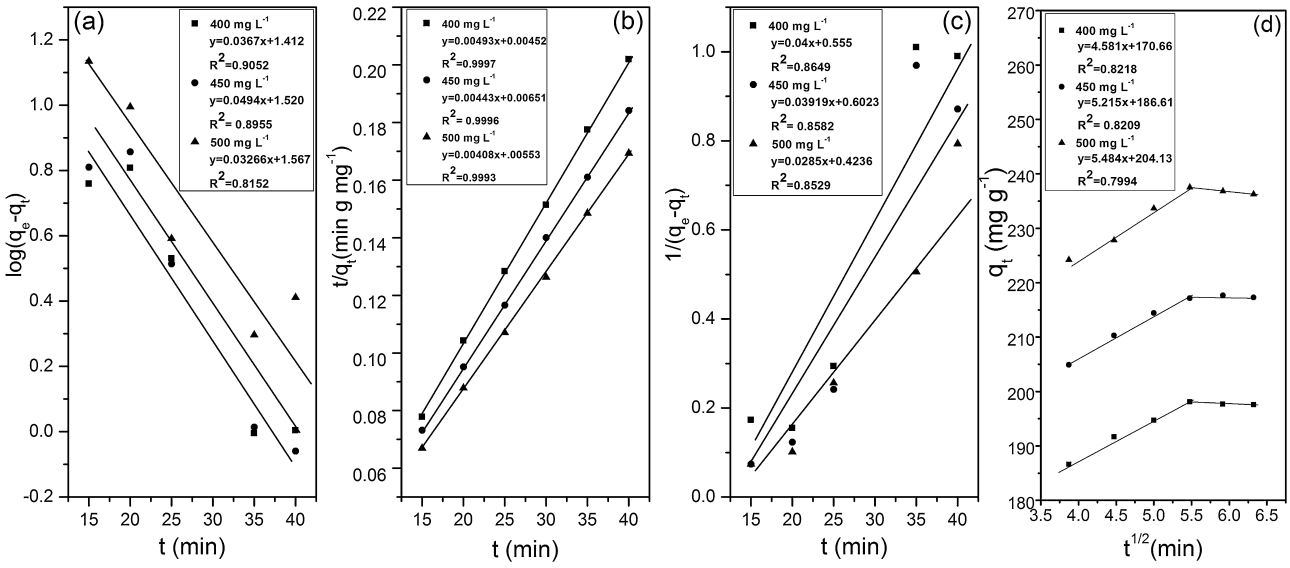

Fig. 4. Kinetic modeling of adsorption of MG on AP-g-PAA 5 using (a) pseudo-first-order, (b) pseudo-second-order, (c) second order and (d) intraparticle diffusion models.

3.4.3. *Thermodynamics study*

In order to explicate the feasibility and spontaneous nature of MG uptake studies, the thermodynamic parameters have been evaluated using Vant Hoff's equation:

$$\ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

The change in entropy (ΔS°, J mol^{-1} K^{-1}) and change in enthalpy (ΔH°, J mol^{-1}) were calculated from the intercept and slope of plot between *ln b* vs. $1/T$ (Fig. S5, Supporting Information). Negative ΔG° values (Table S4, Supporting Information) suggest the spontaneous nature of the MG uptake study. It has also been observed that ΔG° values gradually decreased with increase in temperature (Table S4, Supporting Information), suggesting higher rate of MG adsorption at higher temperature. The positive value of enthalpy change (ΔH°) confirmed the endothermic nature of the dye sorption process (Chowdhury et al., 2011). The positive ΔS° values suggested better attraction of MG toward AP-g-PAA 5 as well as increased randomness at the solid-solution interface (Ghorai et al., 2013; Sun et al., 2008).

3.4.4. *Comparative study of adsorption capacity*

Fig. S6, Supporting Information illustrates the comparison of MG uptake capacity using amylopectin and various adsorbents used here. It is evident that all graft copolymers showed better adsorption characteristics than that of neat polysaccharide, which is due to the presence of grafted poly(acrylic acid) chains on polysaccharide backbone. Out of various graft copolymers, AP-g-PAA 5, which is having the highest % GE, showed the maximum MG removal efficiency, mainly because of the presence of longer grafted chains, which would enhance the hydrodynamic volume as well as the hydrodynamic radius in the solution, resulting higher % of adsorption.

The efficacy of AP-g-PAA 5 for MG removal was compared with various reported adsorbents (Table S5, Supporting Information) and it is obvious that the copolymer showed better efficiency (Q_{max}, 352.11 mg g^{-1}) than that of others for MG adsorption. This implies

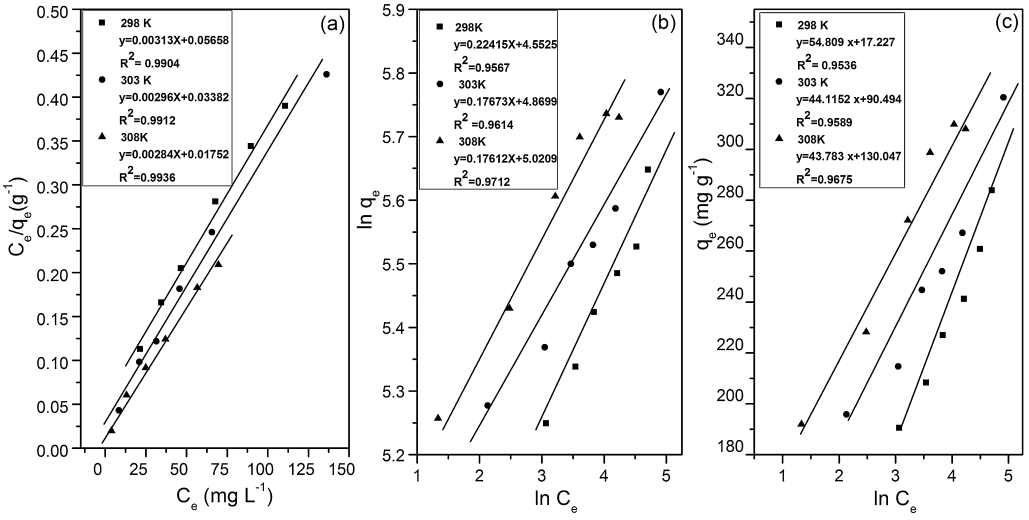

Fig. 5. Isotherm models of the adsorption of MG on AP-g-PAA 5 adsorbent using (a) Langmuir, (b) Freundlich and (c) Temkin isotherm models.

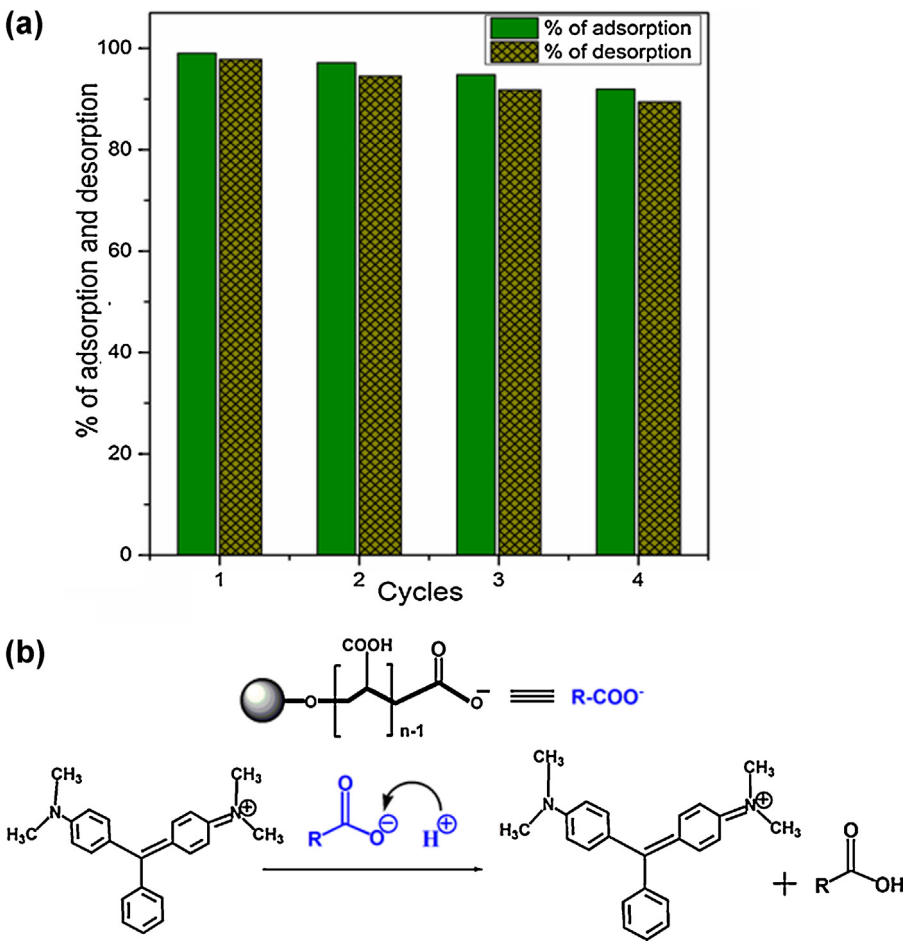

Fig. 6. (a) Simultaneous adsorption–desorption cycles and (b) desorption mechanism of MG using AP-g-PAA 5.

that poly(acrylic acid) grafted with amylopectin have potential excellency to remove MG from aqueous solution.

3.5. Desorption study

An efficient adsorbent should not only possess higher adsorption capacity, but should also exhibit excellent desorption characteristics, which could drastically reduce the overall cost of the adsorbent. Desorption study has been carried out to find out the mechanism of adsorption as well as to determine the reusability of the adsorbent. Desorption experiment was performed using pH 2, 7 and 9 stripping solutions (Fig. 6a). Maximum % desorption was obtained in acidic environment (pH 2: 97.8%) and that of minimum was observed at basic condition (pH 9: 44.5%). The excellent

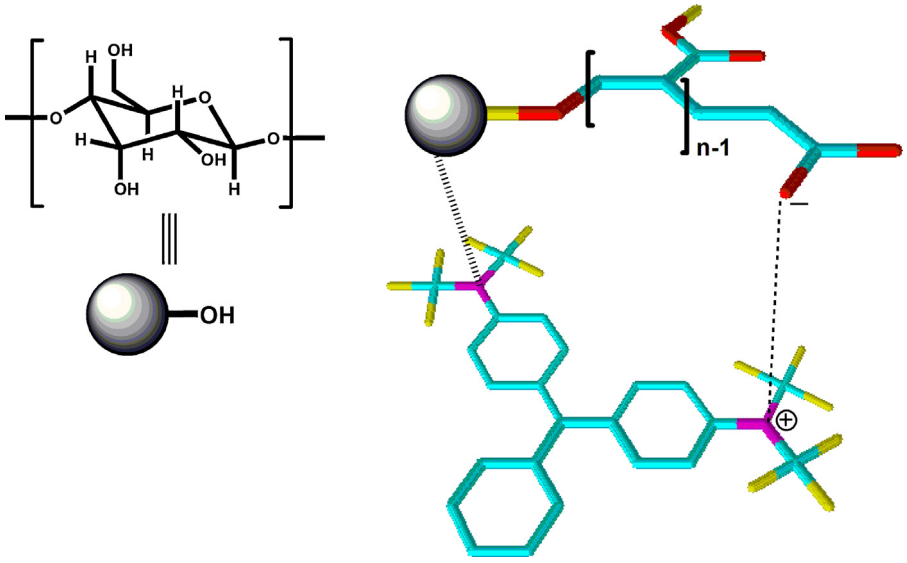

Fig. 7. Adsorption mechanism of MG using AP-g-PAA 5 adsorbent.

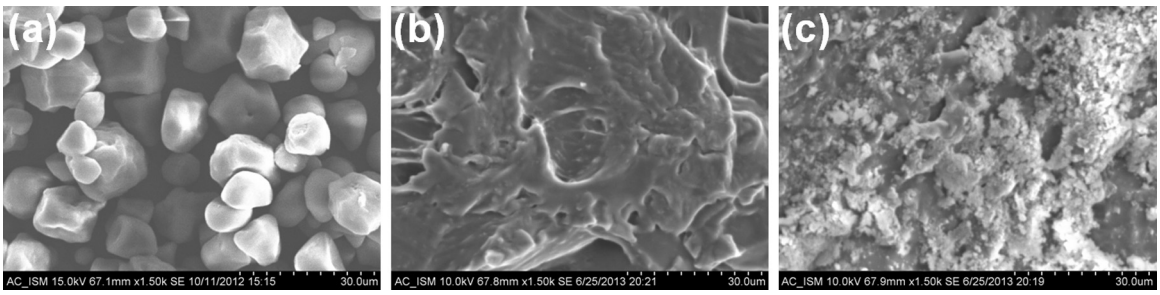

Fig. 8. SEM micrographs (×1.5 K) of (a) amylopectin, (b) AP-g-PAA 5 and (c) MG loaded AP-g-PAA 5.

desorption efficacy of AP-g-PAA 5 in acidic environment reveals that the MG uptake process may follow ion exchange mechanism (Mall, Srivastava, Kumar, & Mishra, 2006). A probable desorption mechanism has been shown in Fig. 6b. It has also been observed that ~89.5% MG was desorbed after 4th cycle (Fig. 6a), which confirmed the excellent regeneration capacity of the copolymer.

3.6. Adsorption mechanism

Various factors including dye structure, surface chemistry of copolymer as well as the interaction between MG and copolymer affect significantly on dye adsorption efficacy. FTIR spectra of AP-g-PAA 5 (Fig. 1b), MG (Fig. 1c) and MG loaded adsorbent (Fig. 1d) have been performed to find the adsorption mechanism. The FTIR spectrum of MG loaded AP-g-PAA 5 exhibits the characteristic peaks of —OH stretching (3465 cm^{-1}) as well as COO^- asymmetric stretching (1569 cm^{-1}). Interestingly, it has been observed that the carbonyl absorption of —COOH groups shifted from 1724 cm^{-1} to 1721 cm^{-1}, COO^- symmetric stretching vibrations of —COOH groups shifted from 1452 cm^{-1} to 1402 cm^{-1} and —OH stretching band shifted from 3475 cm^{-1} to 3465 cm^{-1}. This suggests that electrostatic as well as H-bonding interaction may predominate between the active sites of MG and the —OH as well as $—COO^-$ groups of adsorbent as shown in Fig. 7. The SEM study has also been performed to study the morphological feature and surface characteristics of AP-g-PAA 5 before (Fig. 8b) and after MG adsorption (Fig. 8c). It is apparent from the SEM micrograph (Fig. 8c) that the adsorption of MG leads to the appearance of the white layer, which is due to the major deposition of dye molecules on the adsorbent surface. This signifies about the physical interaction between the adsorbate and adsorbent. Further, salt effect (Fig. 3c) revealed that with the increase in ionic strength, adsorption efficiency gradually decreased, suggesting electrostatic attraction between the positively charged MG and negatively charged adsorbent. Excellent regeneration characteristics of modified amylopectin suggest that ion exchange might be a probable mechanism for MG uptake (Roy, Chakraborty, Kundu, Adhikari, & Majumder, 2013). Thus it is believed that mainly electrostatic interaction is involved in the adsorption process, however, H-bonding interaction may also play a part in adsorption phenomenon.

Additionally surface adsorption, mass transport and consecutive diffusion process also play an important role in adsorption process (Crini et al., 2007; Mahmoodi, 2011; Sekhar et al., 2009). Rapid adsorption of MG indicates that surface adsorption is predominating through strong electrostatic interaction between oppositely charged adsorbate and adsorbent. Further, the copolymer network might be facilitating the mass transport and diffusion process as the carboxylate groups (present in the grafted chains) are hydrophilic in nature. Thus it is expected that intraparticle diffusion may also take place and somehow control the MG adsorption process. Finally, it has been observed that MG uptake using AP-g-PAA follows Langmuir isotherm, suggesting monolayer adsorption of MG on the homogeneous surface of copolymer.

4. Conclusion

From the experimental observations, it can be concluded that poly(acrylic acid) grafted amylopectin based biodegradable adsorbent showed excellent potential for removal of toxic MG from aqueous solution. In comparison to existing systems, the graft copolymer demonstrates better adsorption efficiency as well as good regeneration characteristics and is expected to be a powerful alternative to the literature known adsorbents for the separation of toxic MG from aqueous solution.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.04.042.

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