

Adsorption characteristics of humic acid-immobilized amine modified polyacrylamide/bentonite composite for cationic dyes in aqueous solutions

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Abstract

Humic acid-immobilized amine modified polyacrylamide/bentonite composite (HA-Am-PAA-B) was prepared and used as an adsorbent for the adsorption of cationic dyes (Malachite Green (MG), Methylene Blue (MB) and Crystal Violet (CV)) from aqueous solutions. The polyacrylamide/bentonite composite (PAA-B) was prepared by intercalative polymerization of acrylamide with Na-bentonite in the presence of *N,N'*-methylenebisacrylamide as a crosslinking agent and hexamethylenediamine as propagator. PAA-B was subsequently treated with ethylenediamine to increase its loading capacity for HA. The surface characterizations of the adsorbent were investigated. The adsorbent behaved like a cation exchanger and more than 99.0% removal of dyes was detected at pH range 6.0–8.0. The capacity of HA-Am-PAA-B was found to decrease in the following order: MG > MB > CV. The kinetic and isotherm data were interpreted by pseudo-second order rate equation and Freundlich isotherm model, respectively. Experiments were carried out using binary solute systems to assess the competitive adsorption phenomenon. The experimental isotherm data for each binary solute combination of MG, MB and CV were analyzed using Sheindrof-Rebhun-Sheintuch (SRS) (multicomponent Freundlich type) equation.

Key words: humic acid; polymer/clay composite; dye adsorption; isotherm; regeneration

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Introduction

Direct discharge of dye effluents into aquatic environment may cause the formation of toxic carcinogenic breakdown products that affect aquatic biology and humans. Thus, dyes in wastewaters have to be removed before they are discharged into a water body as laws enacted to preserve the aquatic environment are becoming stringent. Adsorption techniques to remove dyes in solution have been widely used. The adsorption capacity of various adsorbents for dyes has been reported in the literature (Pimol *et al.*, 2008) and these include activated carbons, kaolin, lignite, agriculture waste, waste coir pith, zeolites, clay minerals and chitosan. In clay minerals, even though bentonite is the most commonly employed adsorbent for water treatment, their aggregation nature under varying conditions of temperature and electrolytes hamper its large scale applications. The polyacrylamide molecules were found to be intercalated into the lamina of clay in bimolecular layers. Polyacrylamide hydrogel-bentonite composite systems create greater complexity, in particular greater strength and reduced production cost. These materials may exhibit more properties of an effec-

tive adsorbent than polymer and clay individually. Moreover, by introducing suitable functional groups, adsorption capacity of the polymer/clay composites could be further enhanced (Ulusoy *et al.*, 2003). Humic acid (HA) is one of the major components of humic substances which contain both hydrophilic and hydrophobic molecules as well as phenolic, carboxyl and hydroxyl groups connected to the skeleton of aliphatic or aromatic units. Because of the deprotonation of these carboxylic and phenolic groups in weakly acidic to basic media, HA has negative charge and enhances the adsorption of cations through electrostatic interactions. Recently, our group proposed the immobilization of HA onto zirconium pillared clay to enhance the adsorption potential towards the cationic dyes (Vinod and Anirudhan, 2003). It has been found that aminofunction in adsorbent materials provide novel binding properties for HA (Deng and Bai, 2004). In the present study, a new polyacrylamide/bentonite composite with amine functionality was prepared by direct polymerization technique and is allowed to bind HA and is further applied as an adsorbent for the removal of cationic dyes such as Malachite Green (MG), Methylene Blue (MB) and Crystal Violet (CV) from aqueous solutions.

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1 Materials and methods

1.1 Adsorbent material

The Bentonite (B) sample, used in the present study as the starting material to prepare polymer/clay composite was supplied by Fluka, Switzerland. Acrylamide (AA), *N,N'*-methylenebisacrylamide (MBA), $K_2S_2O_8$ and ethylenediamine (en) were obtained from E. Merk India Ltd. *NNN'N'N'N'*-hexamethylenediamine (HMD) was purchased from Fluka, Switzerland and sodium salt of HA from Sigma Aldrich (Germany). All other chemicals were of analytical grade and were not purified prior to use. The basic dyes (Malachite Green (MG), Methylene Blue (MB) and Crystal Violet (CV)) used in this study as such are cationic since they possess an over all positive charge when ionized in solution. They were supplied by E. Merk, India Ltd. and were used without purification.

1.2 Preparation of amine-modified polyacrylamide-bentonite composite

A 10-g of raw bentonite was transformed into Na-bentonite (Na-B) by treating with 1 L of 1.0 mol/L NaCl solution for 12 h to replace all exchangeable cations with Na^+ , then centrifuged and rinsed several times with distilled water until Cl^- was free. The product was dried at 105°C, ground and sieved to separate the material into 80–230 mesh size range. For the homogenous suspension of 10 g of Na-B in 500 mL distilled water, 15 g of AA in 50 mL distilled water was added in and stirred for 2 h. To this mixture, 1.6 g MBA and 500 mg $K_2S_2O_8$ followed by 0.5 mL HMD was added to propagate the polymerization and then heated in a water bath at 60°C. The polymer-clay composite obtained was then washed with hot water to eliminate homopolymer. It was dried at 60°C for 24 h and the product hereafter designated as polyacrylamide-bentonite (PAA-B). To introduce the amine functionality in PAA-B, 10 g of PAA-B was heated with en (50 mL) at 80°C, at pH 11.0 for 4 h. After the reaction, en incorporated PAA-B (Am-PAA-B) was separated from the solution and washed with water until the filtrate was free from en, as indicated by the absence of any blue colour with ninhydrine reagent. The product, Am-PAA-B was dried at 70°C and sieved to 80–230 mesh size of particles (average diameter of 0.096 mm).

1.3 Preparation of humic acid-immobilized Am-PAA-B (HA-Am-PAA-B)

A stock solution of HA (5000 $\mu\text{mol/L}$) was prepared by dissolving required amount of sodium salt of HA in distilled water. Fifty milliliter of 50 $\mu\text{mol/L}$ solution of HA was equilibrated with 0.1 g Am-PAA-B in the pH range 3.0–7.0 for 4 h, centrifuged and the HA concentrations in the supernatant solutions were determined spectrophotometrically using a UV-Visible spectrophotometer (λ_{max} 350 nm, model V-530, Jasco International Co., Ltd., Japan). The results showed that the maximum loading was occurred at an initial pH range 4.0–6.0. Then it was possible to design an operational condition for loading a

maximum amount of HA onto Am-PAA-B based on the adsorption isotherm. Adsorption isotherm was obtained as described above for HA of the desired concentrations (10–400 $\mu\text{mol/L}$) at pH 6.0. With the light of isotherm results, Am-PAA-B (10 g) was suspended in 500 mL (1250 $\mu\text{mol/L}$) HA and the reaction mixture was then continuously stirred for 24 h at room temperature keeping the solution pH 6.0. The product, HA immobilized Am-PAA-B (HA-Am-PAA-B) was filtered and washed with water to remove residual HA. The washing procedure had no effect on the desorption of HA. Then it was dried at 50°C and sieved for particle size of 80–230 mesh and kept in a desiccator for further use. The maximum loading capacity of HA at 30°C was calculated as high as 103.9 $\mu\text{mol/g}$.

1.4 Measurements

The cation exchange capacity (CEC) was determined by the ammonium acetate method (Mackenzie, 1951). The concentration of Na in the solution was determined using a GBC Aventa A 5450 (Australia) atomic absorption spectrophotometer (AAS). The total number of acidic groups and carboxylic groups present in the adsorbent sample was estimated using a conductometric titration method proposed by James *et al.* (1998). A Systronic microprocessor conductivity bridge (model CB-16 s) was used for conductance measurement. The apparent density of the adsorbent samples was determined by specific gravity bottle. A potentiometric method (Ashok *et al.*, 2005) was used to determine the pH of point of zero charge (pH_{pzc}). The scanning electron micrograph analysis of the adsorbents was carried out on the Phillips XC-3CP (Japan) scanning electron microscope.

1.5 Experiments

Adsorption batch experiments were performed by equilibrating 0.1 g of adsorbent with 50 mL dye solutions of predetermined initial concentrations. The initial pH of the solutions was maintained at the required pH value by adding 0.1 mol/L NaOH and HCl. The suspensions were shaken at 200 r/min for 2 h and were centrifuged. The solutions were separated from the adsorbent and analyzed to determine the dye uptake at different pH levels. The determination of dye concentration was done spectrophotometrically by measuring the absorbance before and after treatment at λ_{max} of 662, 591, and 617 nm for MB, CV, and MG, respectively. Since the absorbance was used to determine dye concentration at different pH levels, absorbance scan was performed as a function of pH. Clearly pH dependant absorbance peaks were obtained for each investigated system. The standard linear calibration curves were prepared to match closely the composition of the analyzed solutions. These calibration curves were used to measure the concentrations of the dyes at different pH levels. Samples were diluted with distilled water if the absorbance values exceeded 0.600. For each adsorption experiments, the average of three replicates was reported. The amount of adsorbed dye at equilibrium (q_e) was

calculated from the mass balance (Eq. (1)).

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

where, C_o is the initial concentration in the liquid phase, C_e the liquid phase concentration at equilibrium, V (L) is the volume of the solution and m (g) is the mass of the adsorbent used. In order to determine the competition among various binary solution mixtures batch experiments were performed using 50 mL combined solution containing varied concentration of dyes with 0.1 g of adsorbent in 100 mL stoppered flask. The contents were shaken by a water bath shaker with a constant speed of 200 r/min at 30°C and were withdrawn at appropriate time intervals and filtered. The filtrate was analyzed for dyes using the following Eqs. (2) and (3).

$$C_A = \frac{K_{B2}d_1 - K_{B1}d_2}{K_{A1}K_{B2} - K_{A2}K_{B1}} \quad (2)$$

$$C_B = \frac{K_{A1}d_2 - K_{A2}d_1}{K_{A1}K_{B2} - K_{A2}K_{B1}} \quad (3)$$

where, subscripts A and B represent components in a binary solute system. K_{A1} , K_{B1} , K_{A2} and K_{B2} are the calibration constants for components A and B at λ_1 and λ_2 , respectively. d_1 and d_2 are the optical densities at λ_1 and λ_2 , respectively.

2 Results and discussion

2.1 Characterization of adsorbents

The classical scheme of analysis (Rump and Krist, 1992) gave the chemical composition of bentonite as: 53.81% SiO₂, 18.43% Al₂O₃, 3.76% Fe₂O₃, 2.11% CaO, 1.76% MgO, 0.61% TiO₂, 3.70% Na₂O, 0.18% K₂O and 15.32% loss of ignition. The adsorbents, Na-B and HA-Am-PAA-B were analyzed for a number of physical and surface properties by standard methods. Na-B, Am-PAA-B, and HA-Am-PAA-B display point of charge at pH_{pzc} 3.0, 7.0, and 4.8 respectively, suggesting that HA-Am-PAA-B surface is more positive than that of Na-B and more negative than Am-PAA-B surface, since pH above the value of pH_{pzc} the surface charge of the adsorbent has a negative charge, below that pH the clay has a positive charge. The apparent density of Na-B, Am-PAA-B, and HA-Am-PAA-B was found to be 1.19, 1.59, and 1.71 g/mL, respectively. The total acidity and CEC were found to be 0.43 and 0.39 meq/g, confirm it for Na-B, and 1.28 and 0.83 meq/g for

HA-Am-PAA-B, respectively. The carboxylate group for HA-Am-PAA-B was found to be 0.66 meq/g.

The SEM photographs obtained for Na-B, Am-PAA-B, HA-Am-PAA-B and MB loaded HA-Am-PAA-B are shown in Fig. 1. It can be seen from SEM images that the surface of Na-B is very smooth with fluffy appearance and after polymer insertion reaction, loses its foliated structure and gain more rough surface. The photograph of Am-PAA-B also shows some deformed parts; probably occur due to the reduction in certain crystalline domains of the clay particles. These surface properties of Am-PAA-B favors better adsorption of HA because of an increase in surface area. After HA adsorption, Am-PAA-B has become more porous due to the reduction in amorphous phase associated within Am-PAA-B. It also shows that the surface condition on Am-PAA-B was somewhat swollen during the contact with HA solution. The SEM image of MB loaded HA-Am-PAA-B showed that its surface has still heterogeneous surface, indicating that the dye is adsorbed significantly on HA-Am-PAA-B.

2.2 Stability of HA-Am-PAA-B

The particles of HA-Am-PAA-B are brown in colour and insoluble in water, dilute acids and alkalies. However, it was observed that concentrated alkalies and acids may cause a leaching of HA from the adsorbent as the colour of the adsorbent changed from its original brown to light yellow. A separate series of experiments were performed to determine the influences of pH on the stability of the adsorbent. It was found that there was no leakage of HA from the adsorbent in a pH range 3.0–9.00. However, a small amount of HA leached out from the adsorbent at higher and lower pH ranges as was detected spectrophotometrically in the UV region at 350 nm. The leaching of HA from the adsorbent increased from 9.0% to 23.0% with increasing pH from 10.0 to 12.0. When the pH of the solution decreased from 2.0 to 1.0, the leaching of HA from the adsorbent increased from 7.0% to 11.0%. At pH above 12.0, the leaching of HA increased steeply causing a brown colour of the solution. Since the wastewaters containing cationic dyes are acidic in nature and the optimum pH range for wastewater treatment is 5.0–8.0, a small amount of HA leaching at higher and lower pH ranges may not create any problem in the HA-Am-PAA-B applications.

2.3 Effect of pH on dye adsorption

Batch adsorption studies were carried out to illustrate the effect of solution pH on both Am-PAA-B and HA-Am-

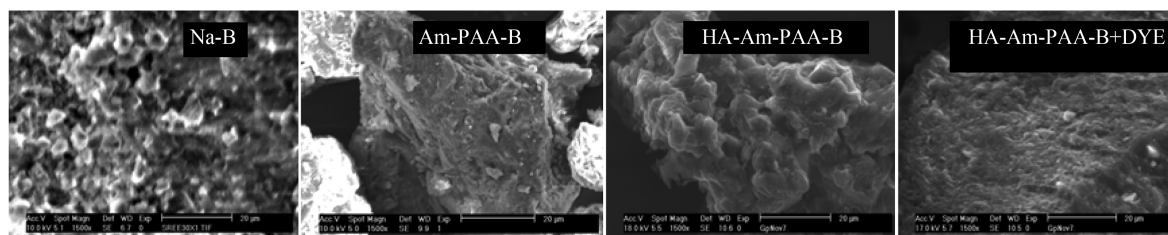


Fig. 1 SEM images of Na-bentonite (Na-B), amine modified polyacrylamide/bentonite composite (Am-PAA-B), HA-Am-PAA-B and MB loaded HA-Am-PAA-B, obtained at 1500× magnification.

PAA-B for dye removal. All three dyes studied, i.e., MG, MB and CV are shown very little adsorption with Am-PAA-B compared to HA-Am-PAA-B (data not shown), and hence we continued removal studies of dyes with HA-Am-PAA-B only.

As shown in Fig. 2, dye adsorption is well dependent on medium pH. The removal capacity of HA-Am-PAA-B increased with increase in solution pH, reached a maximum at pH 6.0, and continued the same maximum value up to pH 8.0. All the three dyes found to follow the similar trend with low percentage of removal at very low pH. At pH 6.0, the maximum adsorption onto HA-Am-PAA-B for 200 $\mu\text{mol/L}$ initial dye concentration was 99.7% for MG, 99.3% for MB, and 98.8% for CV which decreased to 84.0% for MG, 78.1% for MB, and 74.3% for CV when initial dye concentration increased to 400 $\mu\text{mol/L}$. The adsorption of these cationic dyes from aqueous solution onto HA-Am-PAA-B is primarily influenced by the surface charge on the adsorbent. pH_{pzc} for HA-Am-PAA-B was 4.8. At pH above this value the surface of the adsorbent has a negative charge and it facilitated the electrostatic interaction with the cationic dyes. The low adsorption of dyes at very low pH value is due to the protonation of carboxylic groups on the adsorbent surface. Therefore, for pH below 4.8, electrostatic repulsion exists between the positively charged surface and the positively charged dye molecules.

It is worthy to note that the sorption of dyes onto HA-Am-PAA-B decreases the final pH. When the initial pH

of the reaction mixture varied between 5.0 and 8.0, the final pH of the reaction mixture remained between 4.0 and 6.7 for MG, 4.4 and 7.2 for MB, and 4.7 and 7.3 for CV for an initial concentration of 200 $\mu\text{mol/L}$. Similarly for an initial concentration of 400 $\mu\text{mol/L}$, the final pH of the reaction mixture remained between 3.4 and 6.1 for MG, 4.0 and 6.7 for MB and 4.2 and 6.9 for CV when the initial pH of the reaction mixture was varied between 5.0 and 8.0. This decrease in pH was mainly due to ion exchange contribution in the adsorption process. It is well known that the oxygen containing functional groups on the solid adsorbent surface play an important role in the cationic dye adsorption. HA-Am-PAA-B has abundant oxygen containing functional groups such as carboxylic, carboxylic in lactone-like binding structure, phenolic hydroxyl and carbonylic groups (Anirudhan *et al.*, 2008). It is thus considered that the adsorption of cationic dyes releases H^+ from the surface functional groups of HA-Am-PAA-B by an ion exchange mechanism and resulting in a decrease in solution pH at equilibrium. The adsorption capacities of HA-Am-PAA-B for various dyes decreased in the order of $\text{MG} > \text{MB} > \text{CV}$. A similar trend in variation was reported by Basar (2006) for the adsorption of MG, MB, and CV onto activated carbon. There were many factors responsible for this difference in dye uptake, such as different dyes will experience different physical and electrostatic forces according to their structure, molecular size and functional groups.

2.4 Adsorption kinetics

2.4.1 Single solute adsorption kinetics

Figure 3 illustrates the effects of contact time on each dye adsorption onto HA-Am-PAA-B as obtained from batch experiments. Results showed that adsorption occurred rapidly in the beginning and slowly reached equilibrium at about 1 h. Thus a 3-h contact time is recommended in all experiments. The largest amount of (> 90.0%) dye is removed by the adsorbent within the first 15 min due to surface mass transfer. Because of the presence of MBA crosslink units in polymer/clay composite, the adsorbent possesses a high swelling capacity and consequently its network is sufficiently expanded to allow a fast diffusion process for the dye molecules (Crini *et*

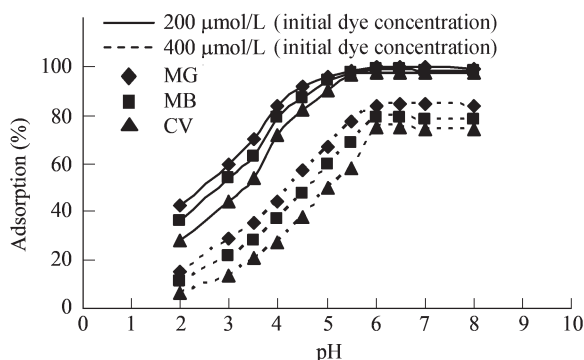


Fig. 2 Effect of pH on the adsorption of dyes onto HA-Am-PAA-B. Adsorbent dosage: 2 g/L; equilibrium time: 3 h.

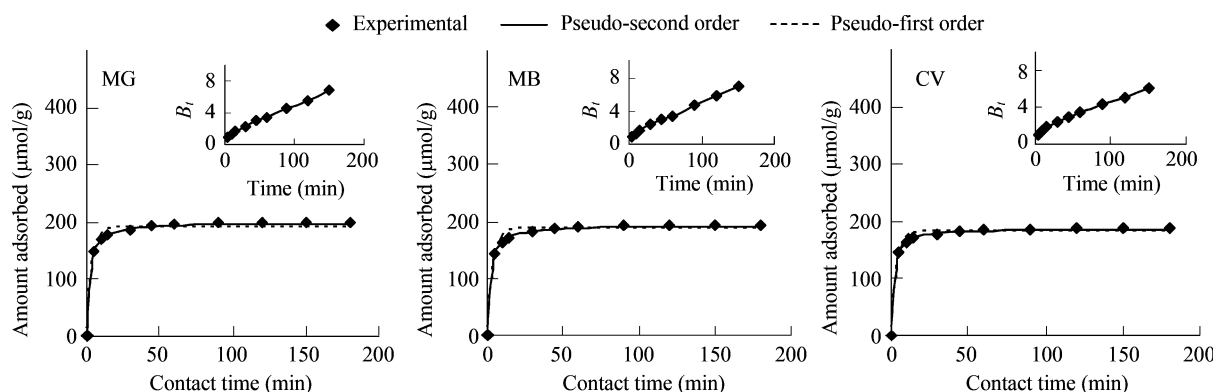


Fig. 3 Adsorption kinetics of dyes onto HA-Am-PAA-B, fitted to pseudo-first order and pseudo-second order equations. The inset is a plot of B_t versus time for various dyes adsorption onto HA-Am-PAA-B.

al., 2007). This expanded network of the adsorbent favors the interaction between the cationic dye molecules and the most favorable adsorption sites (carboxylic groups) on the adsorbent surface. The rapid adsorption phenomenon is advantages in process application since the shorter contact time effectively attains for a smaller size of the contact equipment, which in turn directly affects both the capacity and operation cost of the process (Mouzdahir *et al.*, 2007). The uptake of dyes after equilibrium was 199.4 $\mu\text{mol/g}$ (99.7%) for MG, 193.4 $\mu\text{mol/g}$ (96.7%) for MB, and 187.5 $\mu\text{mol/g}$ (93.8%) for CV with an initial dye concentration of 400 $\mu\text{mol/L}$.

In order to find out which model is the best fit in describing the adsorption kinetics of dye on adsorbent, using nonlinear regression analysis, the generally applied models, i.e., pseudo-first order and second order were tested. In comparison with pseudo-first order, second order kinetic expression proposed by Ho and Mc Kay (1999) yielded the best results for experimental kinetic data in HA-Am-PAA-B-dye systems with higher values of correlation coefficients ($R^2 > 0.995$) and lower chi-square values ($\chi^2 < 2.0$). Considering the adsorption behavior of dyes from liquid phase to solid phase as surface complexation reaction, the specific rate constant for the process was calculated by the following Ho and McKay pseudo-second order rate expression (Eq. (4)).

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

where, q_t ($\mu\text{mol/g}$) and q_e ($\mu\text{mol/g}$) are the amount adsorbed at time t and equilibrium respectively, k_2 ($\text{g}/(\text{mg} \cdot \text{min})$) is the pseudo-second order rate constant. The resulted pseudo-second order rate constant for 400 $\mu\text{mol/L}$ of MG, MB, and CV adsorption via HA-Am-PAA-B were 2.97×10^{-2} , 2.95×10^{-2} , and 2.64×10^{-2} $\text{g}/(\text{mg} \cdot \text{min})$. This supports the assumption behind the model that the surface complexation may be the rate-limiting step involving valence forces through sharing or exchanging of electron between adsorbent and adsorbate (Ho *et al.*, 2004). In Fig. 3, the best agreement of the experimental kinetic data with the pseudo-second order kinetic model can also be observed.

For a solid-liquid adsorption process, the solute transfer is usually characterized by either film diffusion or intraparticle diffusion or both. In order to examine the controlling mechanism of the adsorption process, the Boyd equation (Eq. (5)) (Rauf *et al.*, 2007) was used to test the

experimental data.

$$F = 1 - \frac{6}{\pi^2} \exp(-B_t) \quad (5)$$

where, F is the fractional attainment of equilibrium at time t (i.e., q_t/q_e) and B_t is a mathematical function of F . The values of B_t were calculated using the following equation (Eq. (6)).

$$B_t = -0.4977 - \ln(1 - F) \quad (6)$$

The inset in Fig. 3 shows the B_t versus t plots for the three dyes. The plots are used to test whether linear behavior is obtained and whether the lines pass through zero, which is useful to identify the film diffusion or intraparticle diffusion. If the plot is a straight line passing through the origin, then the adsorption is governed by a particle-diffusion mechanism, otherwise it is governed by film diffusion. As shown in Fig. 3, the plots were not linear, indicating that film diffusion mainly governs the rate-limiting process.

2.4.2 Bi-component adsorption kinetics

In binary systems, each dye compete with others for the limited number of adsorption sites of the adsorbent and resulted in reduced adsorption compared to their single solute solutions. The variations of adsorption density of each dye in presence of other in each binary system are shown in Table 1. Figure 4 shows the adsorption kinetics of 800 $\mu\text{mol/L}$ of MG in the presence of varying concentrations of CV (200–2400 $\mu\text{mol/L}$) and CV in the presence of MG (200–2400 $\mu\text{mol/L}$) in bi-component solutions using the same amount of HA-Am-PAA-B. MG had posed greater interference on the adsorption of CV than CV on MG adsorption. When concentration of competitive ion increased, adsorption efficiency of CV went down than that of MG. Similar kinetic plots were obtained for the MG-MB and MB-CV systems (figures not shown). The results show that the adsorption of MG is significant than CV and MB in MG-CV and MG-MB binary systems, respectively; and the adsorption of MB is significant than CV in MB-CV binary systems which are in accord with the previous results obtained from single solute kinetics. The results were likely due to a higher adsorption affinity of MG onto HA-Am-PAA-B which led to MG substitution for MB and CV adsorbed onto the adsorption sites.

2.5 Adsorption isotherm

2.5.1 Single solute equilibrium adsorption

Figure 5 shows the amount of adsorption at different dye concentrations in single systems. The dye adsorption was

Table 1 Competitive adsorption of MG, CV and MB

CV or MB ($\mu\text{mol/L}$)	MG adsorption ($\mu\text{mol/g}$) ^a		CV or MG ($\mu\text{mol/L}$)	MB adsorption ($\mu\text{mol/g}$) ^b		MB or MG ($\mu\text{mol/L}$)	CV adsorption ($\mu\text{mol/g}$) ^c	
	With CV	With MB		With CV	With MG		With MB	With MG
0	373.1	373.1	0	356.2	356.2	0	308.7	308.7
200	347.2	341.9	200	341.2	313.7	200	285.6	275.3
800	329.6	311.2	800	317.6	290.3	800	260.0	238.8
1600	305.0	288.6	1600	296.8	260.3	1600	238.1	187.4
2400	283.4	266.3	2400	276.6	250.7	2400	211.5	137.6

^{a, b, c} Initial MG, MB, and CV concentrations are all 800 mol/g.

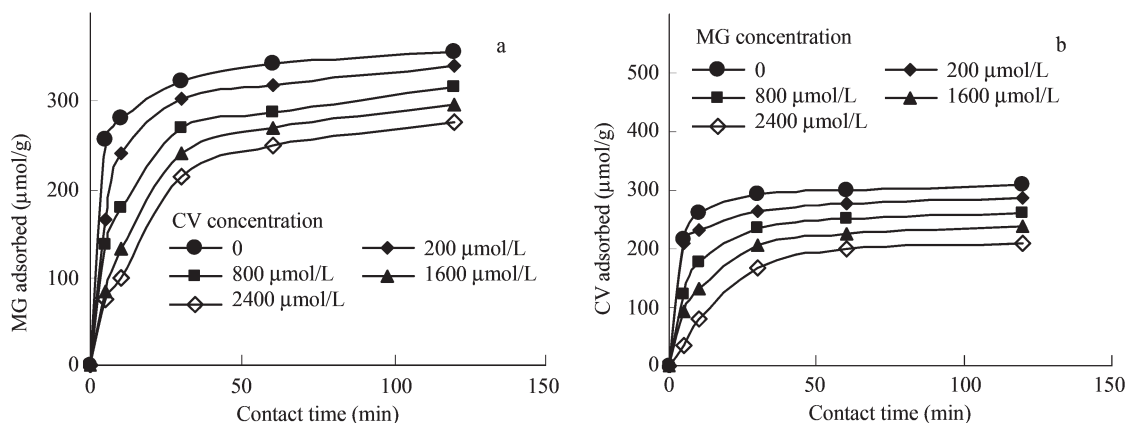


Fig. 4 Kinetic study of competitive adsorption of MG in the presence of CV (a) and CV in the presence of MG (b). Both initial MG and CV concentrations are 800 $\mu\text{mol/L}$.

affected by initial dye concentrations as shown in Fig. 5. With increasing concentrations, the dye adsorption by HA-Am-PAA-B increased strongly and then slightly leveled off with small rise of adsorption. Adsorption isotherm is of much importance in adsorption techniques as it provides approximate estimation of the adsorption capacity of the adsorbent. Langmuir (Eq. (7)), Freundlich (Eq. (8)) and Dubinin-Radushkevich (D-R) (Eq. (9)) adsorption isotherms were investigated.

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (7)$$

$$q_e = K_F C_e^{1/n} \quad (8)$$

$$q_e = q_m (\varepsilon^2)^{-\beta} \quad (9)$$

where, q_e ($\mu\text{mol/g}$) is the adsorption capacity and C_e ($\mu\text{mol/L}$) is equilibrium concentration of the adsorbed species. Q^0 ($\mu\text{mol/g}$) and b ($\text{L}/\mu\text{mol}$) are Langmuir constants related to the adsorption capacity and energy/intensity of adsorption. The Freundlich constants K_F and $1/n$ are related to the adsorption capacity and heterogeneity factors respectively. q_m is D-R constant related to theoretical saturation capacity and ε is the Polanyi potential and can be calculated using the formula, $RT \ln(1 + 1/C_e)$.

All these isotherm constants were calculated using a non-linear optimization method and the results are presented in Table 2.

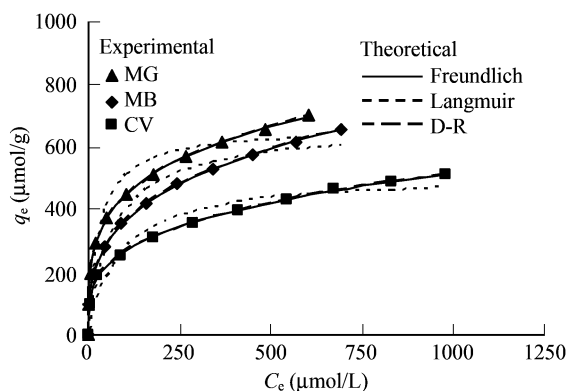


Fig. 5 Comparison of the experimental and model fits of the Langmuir, Freundlich and D-R isotherms for the adsorption of dyes onto HA-Am-PAA-B. Adsorption dosage: 2 g/L; temperature: 30°C; initial pH: 6.0.

The values of R^2 and χ^2 show that the adsorption process is fitted to the Langmuir, D-R and Freundlich equations, of which the latter gives the best correlation indicating heterogeneous nature of the adsorbent. Figure 5 also shows a comparison between the theoretical Langmuir, Freundlich and D-R isotherms and the experimental data. The Freundlich model shows a better fit to adsorption data than the Langmuir and D-R models. The adsorption coefficient K_F in Table 4 is related to the capacity of the adsorbent for the dye and $1/n$ is a function of the strength of adsorption. The larger value of K_F , the larger is the adsorption capacity and the smaller value of $1/n$, the stronger is the adsorption affinity. The value of $1/n$ ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Hameed *et al.*, 2007). The values of K_F and $1/n$ obtained in this present study suggest that dyes are favorably adsorbed by HA-Am-PAA-B. The adsorption capacity (K_F) obtained for MG was higher than the values found for MB and CV, showing the following capacity order $\text{MG} > \text{MB} > \text{CV}$. Dadhaniya *et al.* (2006) reported that polymer based hydrogels presented the order of affinity for cationic dyes $\text{MG} > \text{MB} > \text{CV}$, which agrees with the one observed in this study.

Table 2 Sorption isotherm parameters

Isotherm	MG	MB	CV
Freundlich			
K_F	142.1	89.7	71.8
$1/n$	0.248	0.304	0.385
R^2	0.999	0.999	0.999
χ^2	0.87	1.36	1.33
Langmuir			
Q^0 ($\mu\text{mol/g}$)	656.5	648.4	510.4
b ($\text{L}/\mu\text{mol}$)	0.034	0.015	0.012
R^2	0.984	0.974	0.934
χ^2	4.5	4.2	9.1
D-R			
q_m ($\mu\text{mol/g}$)	1009.7	979.2	670.4
β	0.128	0.154	0.144
R^2	0.977	0.963	0.981
χ^2	6.7	5.7	8.2

2.5.2 Binary component equilibrium adsorption

The MG, MB, and CV adsorption from aqueous solutions in a concentration range 200–1000 $\mu\text{mol/L}$ at pH 6.0 by HA-Am-PAA-B were determined under competitive conditions, i.e., simultaneous adsorption from solutions containing all of the dyes, as described in the experimental section. Figure 6 shows the competitive adsorption isotherm of MG by HA-Am-PAA-B in the presence of varied concentrations of CV. It is seen that, with increased concentration of CV, individual adsorption of both MG and CV is reduced correspondingly to their single solute solution, but the degree of suppression was greater for CV adsorption. Similar studies were carried out for MG-MB and MB-CV systems and in all cases shape of competitive isotherm curves (figures not shown) are similar with that observed in MG-CV system (Fig. 6). In MG-MB system, the presence of MG put grater suppression to MB adsorption than MB to MG adsorption by HA-Am-PAA-B. Similarly in MB-CV system, the greater competition was from MB molecules than CV and hence increasing the equilibrium MB concentration resulted in less CV adsorption.

In the present study, in order to illustrate the competitive adsorption we used the Sheindrof-Rebhun-Sheintuch (SRS) equation, a multicomponent Freundlich type equation, which is based on the assumption of exponential distribution of adsorption energies available for each solute (Sheindrof *et al.*, 1981).

A general form of SRS equation is written as Eq. (10).

$$(q_e)_i^j = K_{Fi} C_{ei} \left(\sum a_{ij} C_{ej} \right)^{((1/n_i)-1)} \quad (10)$$

where, $(q_e)_i^j$ is the amount of solute i adsorbed per unit weight of adsorbent in the presence of solute j , K_{Fi} and $1/n_i$ are the single component Freundlich constant and exponential term for solute i , respectively, C_{ei} and C_{ej} are the equilibrium concentrations of solute i and j , respectively, and a_{ij} is the competitive coefficient. For binary solute systems the Eq. (10) can be presented in the following form.

$$(q_e)_i^j = K_{Fi} C_{ei} (C_{ei} + a_{ij} C_{ej})^{((1/n_i)-1)} \quad (11)$$

In order to represent the binary component competitive adsorption isotherm data the following linearised forms of SRS equations (Eqs. (12) and (13)) are used.

$$\frac{C_{ei}}{C_{ej}} = \left(\frac{B_i}{C_{ej}} \right) - a_{ij} \quad (12)$$

$$\frac{C_{ej}}{C_{ei}} = \left(\frac{B_j}{C_{ei}} \right) - a_{ji} \quad (13)$$

where, $B_i = (K_{Fi} \frac{C_{ei}}{q_{ei}})^{\frac{n_i}{n_i-1}}$ and a_{ij} and a_{ji} , the competitive coefficients can be obtained by plotting $\frac{C_{ei}}{C_{ej}}$ against $\frac{B_i}{C_{ej}}$ and $\frac{C_{ej}}{C_{ei}}$ against $\frac{B_j}{C_{ei}}$, respectively.

The competitive coefficients obtained by applying the SRS equation to each of six binary solute combinations are listed in Table 3. It can be seen from Table 3 that the magnitude of MG competition on CV adsorption is significant with a competitive coefficient of 0.768 than CV competition on MG adsorption with a competitive coefficient of 0.054 which is in agreement with the quantitative observation made in this study. Figure 7 shows the SRS

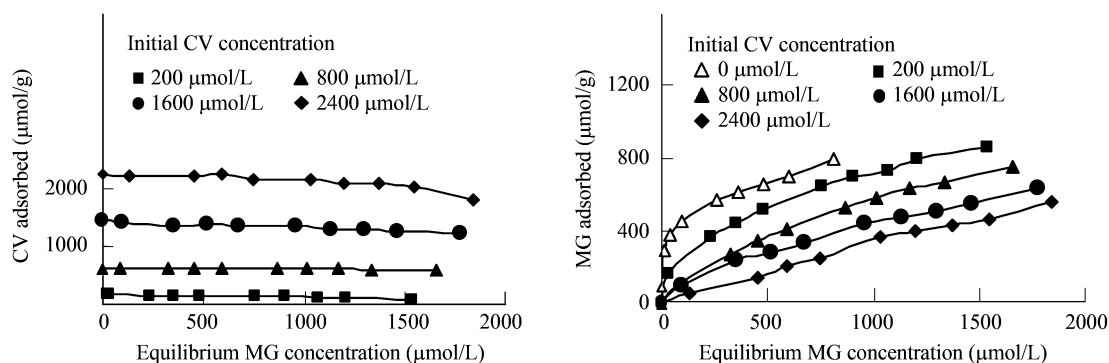


Fig. 6 Competitive adsorption isotherm of MG or CV in the presence of CV or MG.

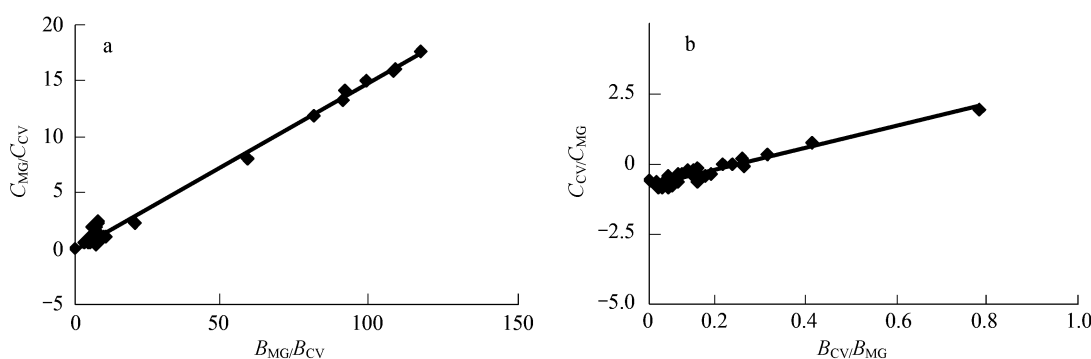


Fig. 7 SRS competitive adsorption isotherm plots for MG in presence of CV (a) and CV in presence of MG (b).

plot for MG-CV system. The high value of correlation coefficient $R^2 > 0.99$, indicates the good positive relationship with the experimental data and suggest the applicability of the SRS equation in the present systems.

Table 3 Competitive coefficients for binary solute systems, derived by the application of Sheindrof-Rebhun-Sheintuch equation

Parameter	Dye system		
	MG + CV	MG + MB	MB + CV
Competitive coefficient			
a_{ij}	0.054	0.114	0.307
a_{ji}	0.768	0.555	0.527
Correlation coefficient			
R^2	0.992	0.988	0.994

3 Conclusions

This study demonstrated the removal potential of humic acid immobilized polyacrylamide bentonite composite with amine functionality (HA-Am-PAA-B) for cationic dyes (MG, MB, and CV) from their single and binary component solutions. The effect of pH, initial dye concentration and agitation time on adsorption was investigated. The maximum dye removal was observed at the initial pH range 6.0–8.0. The process of adsorption was very fast and equilibrium was reached at 1 h. The kinetics of dyes adsorption onto HA-Am-PAA-B followed the pseudo-second order rate model. Film diffusion mechanism was found to be the rate-limiting step. The Freundlich isotherm model showed a somewhat better fit than did the Langmuir and D-R models for adsorption of dyes onto HA-Am-PAA-B. The adsorption capacity of HA-Am-PAA-B was decreased in the order: MG > MB > CV. Bi component dye adsorption studies were also in accordance with this order. Sheindrof-Rebhun-Sheintuch (SRS), a multicomponent Freundlich type equation for each solute combination of MG, MB and CV was useful for describing the degree of competitive interaction of dyes with HA-Am-PAA-B. Results of the experiments demonstrated that HA-Am-PAA-B was successful for the removal of basic dyes from aqueous solutions.

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