



Equilibrium and Kinetic Studies on the Removal of Acid Red-14 from Aqueous Solutions Using PSMA

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Abstract

The use of low-cost and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. In this study, not hydrolyzed poly(styrene-alternative-maleic anhydride) (PSMA) polymer have been used as new synthetic adsorbent to removal of acid red-14 dye from aqueous solutions (industrial wastes). Batch sorption studies have been carried out to determine the effect of agitation time, pH, adsorbent dose, and initial concentration of the sorbate and temperature. The effect of electrolyte interference such as Na⁺ and Cl⁻ on dyes removal efficiency was investigated. The acid red 14 dye showed maximal amount of sorption capacity as 5.12 mg/g at pH 6.1 and 25 °C. Equilibrium data were fitted with Langmuir and Freundlich isotherms to find the best fit, and it was found that the adsorption of this dye on adsorbents particles are monolayer and correspond to the Langmuir isotherm. Adsorption kinetics were investigated using pseudo-first-order and pseudo-second-order rate equations and kinetic data followed the pseudo-second-order rate equation for sorption of this dye on PSMA adsorbent. The application of adsorbents performance was tested with real samples which contain limit exceeded amount of foresaid dyes which had been taken from a Dyeing Factory. This study provides good background to development of dye removal in waste waters by polymeric sorbent.

Keywords Adsorption · Acid red-14 removal · Isotherms · Kinetic · PSMA

1 Introduction

The residual dyes from different sources are considered a wide variety of organic pollutants introduced into the natural water resources or wastewater treatment systems. One of the main sources with severe pollution problems worldwide is the textile industry and its dye-containing wastewaters (i.e., 10,000 different textile dyes with an estimated annual production of 7.105 metric tonnes are commercially available worldwide; 30% of these dyes are used in excess of 1000 tonnes per annum, and 90% of the textile products are used at the level of 100 tonnes per annum or less) (Baban et al. 2010; Robinson et al. 2001;

Soloman et al. 2009). The removal of dyes from textile effluents is currently of great interest (Juang et al. 1996). Among the advanced chemical or physical treatments, adsorption is considered to be superior to other techniques. This attributed to its easy availability, simplicity of design, ease of operation, biodegradability, insensitivity to toxic substances, and ability to treat dyes in more concentrated forms (Dobrowski 2001).

Various types of adsorbents to remove contaminants exist, such as activated carbon (Weber 1972), silica (Feng and Aldrich 2004), and zeolite (Montanher et al. 2005). Daneshvar and his Associates investigated photocatalytic degradation of Acid Red 114(AR-14) (Daneshvar et al. 2003, 2004). Valderama and his Associates investigated to removed Acid red-14 using highly crosslinked polymeric adsorbent, MN300 and Macronet MN200 (Valderrama et al. 2008). Buchen and his associates investigated behavior of absorb acid red 14 by Surface soil (DG06, GSE17200, and GSE17201) in aqueous solutions. Adsorption isotherms showed that the adsorption process is

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better described by Freundlich model and the DG06 has the highest K_F . Kinetics adsorption show pseudo-second model. The review showed that the pH and salt are effective on removal process (Baocheng et al. 2008).

In the present study, PSMA were used as an adsorbent for the removal of Acid Red 114 (AR-14). The materials chosen are available in large quantities in world and at low cost. Effective parameters such as adsorbent dosage, initial dye concentration, electrolyte, pH, temperature, and kinetics studies were carried out to evaluate the adsorption capacity of the PSMA.

Acid Red 14 or C.I. 14720 is a synthetic red food dye from the azo dye group. It usually comes as a disodium salt. It is a red to maroon powder. It is used for the purposes where the food is heat-treated after fermentation. It has E number E122. Some of the foods can be present in are blancmange, marzipan, Swiss roll, jams, preserves, yoghurts, jellies, breadcrumbs, nougat, and cheesecake mixes. It is also present in Oraldene Mouthwash.

2 Materials and Methods

2.1 Preparation of Activated Adsorbents

2 g of maleic anhydride added to a 100-ml flask and then 23.2 mL of freshly distilled styrene added to it. 50 mL of tetrahydrofuran was added to it and the flask for 20 min under nitrogen inert gas bubbles to put up to remove the dissolved oxygen. After 20 min, 0.0197-g benzoyl peroxide is added to the flask, and the reaction was started and continued under inert gas argon for 7 h at 80° C. The contents of the flask were cooled. 100-mL methanol was added until a white precipitate is obtained. The sediment was filtrated by filter paper and was washed using methanol. The precipitate was placed in a 30 °C for 24 h to dry completely. At this point, the white powder copolymer [poly(styrene-alternative-maleic anhydride)] is obtained.

2.2 Procedure and Adsorption Studies

Figure 1 shows the structure of AR-14.

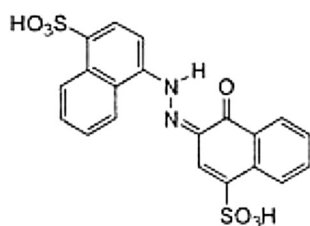


Fig. 1 Structure of AR-14

To study the effect of parameters such as adsorbent dosage, pH, and initial concentration for the removal of color in AR-14, batch experiments were carried out in a thermostatic orbital shaker (Hotplate/Stirrer Model-81) at a constant speed of 175 rpm at room temperature. The adsorption isotherm experiment was carried out by agitating 20-mL dye solutions of various concentrations. After agitation, the dye solutions were separated from the adsorbent by centrifugation for 5 min. Dye concentrations in the supernatant solutions were measured using a UV–Vis spectrophotometer (UV–Vis spectrophotometer—T80+). The effect of initial pH on dye removal was studied over a pH range of 5–9. The initial pH of the dye solution was adjusted by the addition of 0.1 N solution of HCl or NaOH. To find the optimum amount of adsorbent per unit mass of the adsorbate, the dye solution (20 mL) was contacted with different amounts of PSMA till equilibrium was reached. The kinetic experiments were carried out using a known weight of adsorbent and employing AR-14 in the concentration range of 60–100 mg/L in a mechanical stirrer (Hotplate/Stirrer Model-81). The samples were withdrawn at predetermined time intervals and centrifuged. The effect of temperature on the adsorption characteristics was studied by determining the adsorption isotherms at 25, 30, 35, 40, and 50 °C with a fixed dye concentration and dosage. The dye removal percentage and amount adsorbed were calculated using the following relationships:

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

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

$$\text{Amount adsorbed (mg/g)} (q_e) = (C_0 - C_e)(V/m), \quad (2)$$

where C_0 and C_e are, respectively, the initial and equilibrium concentrations of dye (mg/L), m is the mass of the adsorbent (g), and V is the volume of the dye solution (L).

3 Results and Discussion

3.1 Effect of Adsorbent Dosage

The effect of changing adsorbent dosage on the adsorption rate of AR-14 was studied by varying the concentration of the adsorbent from 0.02 to 0.1 g/20 mL while keeping the other experimental conditions constant. The percentage removal of AR-14 versus adsorbent dosage is shown in Fig. 2. An increase in the percentage of adsorption with increasing adsorbent dosage was observed in all the adsorbent. This was due to the availability of more surface functional groups at higher concentrations of adsorbents (Garg et al. 2004). However, the amount of dye adsorbed

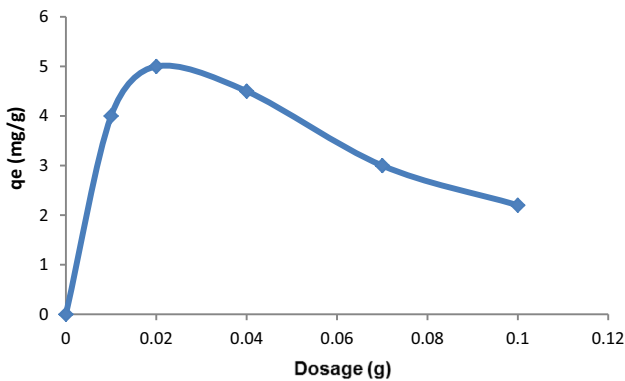


Fig. 2 Effect of temperature on the sorption of AR-14 on PSMA

per unit weight of the adsorbent decreases with increase in dosage, as observed in all the cases. This may be attributed to the aggregation of adsorbent particles at high dosage, which reduces the total surface area of the adsorbent and results in an increase in the diffusion path length (Shukla et al. 2002).

3.2 Effect of Initial pH

The effect of initial pH on the adsorption of dye by PSMA was studied by varying the initial pH of the dye solution from 5 to 9 under constant experimental conditions (as shown in Fig. 3). It is evident from Fig. 3 that adsorbent showed better adsorption capacity at the initial pH of 6.1. AR-14 is polar molecule ($R - SO_3^-$) at low pH. To justify that the acidic and alkaline environments are not suitable, we can say that in the acidic environment, high concentration of hydrogen ions causing to naturalized the dye, and thus, the absorption efficiency decreases. The high concentration of hydroxide ions in the alkaline environment causing to saturate the active sites of the adsorbent, and thus, the absorption efficiency decreases. As the pH of the

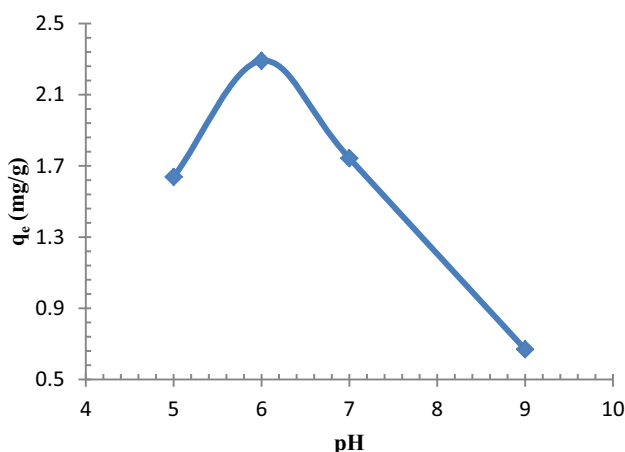


Fig. 3 Effect of pH on the sorption of AR-14 on PSMA

system increases, the number of negatively charged sites is increased. A negatively charged site on the adsorbent does not favour the adsorption of anionic dye molecules due to the electrostatic repulsion. It is known that acid dyes, on dissolution, release colored dye anions into solution. The adsorption of these anionic charged groups onto the adsorbent surface is primarily influenced by the surface functional groups on the adsorbent, which, in turn, is influenced by the solution pH. A similar result was observed for the adsorption of Acid Red 14 by soy meal hull (Arami et al. 2006).

3.3 Effect of Initial Concentration (C_0)

The effect of C_0 on the removal of AR-14 by PSMA is shown in (Fig. 4). With increasing initial concentration of AR-14, PSMA capacity increased due to the availability of large amounts of AR-14 in the absorber mass unit.

3.4 Effect of Temperature

A low temperature was, therefore, more suitable for AR-14 removal, showing that the adsorption was exothermic in nature. An escape of dye molecules from the solid surface to the solution for an increment in temperature can account for this behavior (Fig. 5).

3.5 Effect of Contact Time

Sorption studies of AR-14 onto PSMA were carried at different time intervals (0–60 min) at pH 6.1. Initially, the sorption was rapid and then slows down attaining an equilibrium point, because initially available sites on the surface of sorbent (means the surface is unsaturated) are large to the sorption, and as the contact time increases, it gradually decreases until it attains equilibrium (Wu et al.

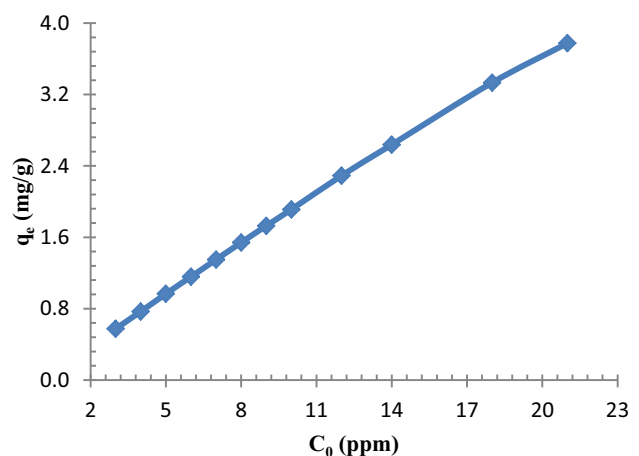


Fig. 4 Effect of C_0 on the sorption of AR-14 on PSMA

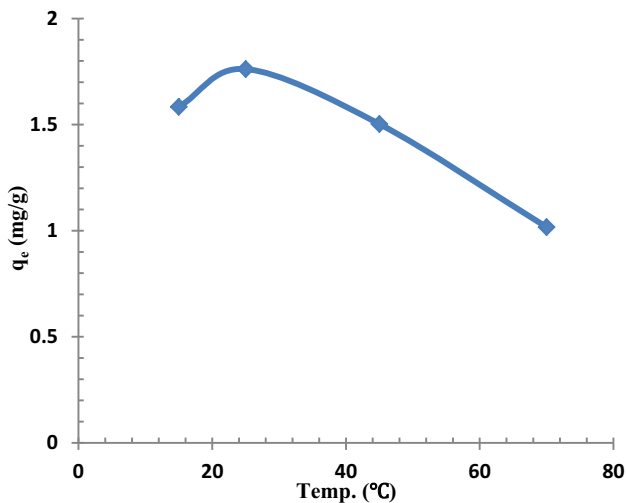


Fig. 5 Effect of time on the sorption of AR-14 on PSMA

2008). Equilibrium time for PSMA was found to be 45 min at 5-g/L initial AR-14 concentration (Fig. 6).

3.6 Effect of Electrolyte

Increased electrolyte can cause to neutralization of the adsorbent surface charge and also compete with the adsorbent material to take over the active sites of adsorbent. Industrial effluents often contain significant amounts of various electrolytes which are, therefore, studied the effect of electrolyte on the removal of colored material in real terms is considered (Ehrlich and Ehrlich 1972). Removal efficiency decreases with increasing electrolyte. This could be due to the neutralization of the adsorbent surface charge and the deactivation of polymer adsorption sites due to the presence of the electrolyte. However, in the

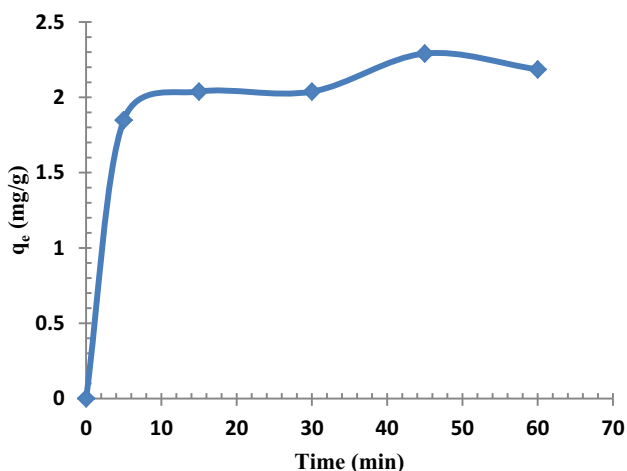


Fig. 6 Effect of adsorbent dosage on the sorption of AR-14 on PSMA

presence of electrolytes yields not much decreased, indicating the possible use of this adsorbent at a higher scale for remove colored material of actual examples of wastewater.

3.7 Adsorption Isotherm

The quantity of dye that could be taken up by an adsorbent is a function of both the concentration of the dye and the temperature. The amount of dye adsorbed is determined as a function of the concentration at a constant temperature, which could be explained by adsorption isotherms. In this study, two isotherms Langmuir (Eq. 3) (Langmuir 1918) and Freundlich (Eq. 5) (Freundlich 1906) were tested:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}, \quad (3)$$

or

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max}} C_e + \frac{1}{K_L Q_{\max}}, \quad (4)$$

$$q_e = K_F C_e^{\frac{1}{n}}, \quad (5)$$

or

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e, \quad (6)$$

where C_e is the concentration of the dye solution (mg/L) at equilibrium, q_e is the amount of dye adsorbed per unit weight of adsorbent (mg/g), K_L is the constant related to the free energy of adsorption (L/mg), and Q_m is the maximum adsorption capacity. K_F is a Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g), and $1/n$ is the adsorption intensity.

The isotherm constants for all the isotherms studied were calculated from the linear form of each model and the correlation coefficients are given in (Table 1). Figure 7

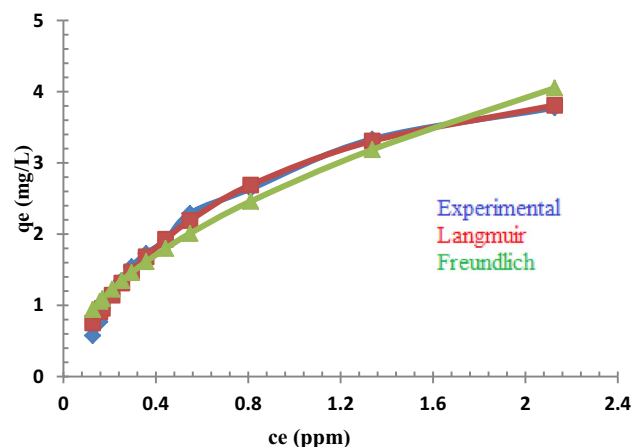


Fig. 7 Adsorption isotherm of the AR-14 on PSMA (pH 12)

shows the comparative fit of Langmuir and Freundlich isotherms with the equilibrium data plotted as q_e versus C_e . From Fig. 7 and the experimental results, it can be seen that the Langmuir model is the best-fit model for the adsorption of AR-14 onto PSMA. From the experimental results, it can be seen that the Langmuir model fits better than the Freundlich model. Moreover, the dimensionless constant R_L lies within the favourable limit. The values of $1/n$ were also found to be between 0 and 1, indicating favourable adsorption of AR-14 on PSMA.

Where q_e is the equilibrium dye concentration on the adsorbent (mol L^{-1}); C_e , the equilibrium dye concentration in solution (mol L^{-1}); q_m , the monolayer capacity of the adsorbent (mg g^{-1}); K_L is the Langmuir constant. Plots of $1/q_e$ vs. $1/C_e$ for the biosorption of dye on to PSMA give a straight line with the slope of $1/q_{\text{max}}$ and intercept $1/q_{\text{max}} \cdot K_L$. The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, R_L defined by the following:

$$R_L = \frac{1}{1 + K_L C_0}, \quad (7)$$

where K_L is the Langmuir constant, C_0 the initial dye concentration (mg/L). R_L values indicate that the type of isotherm is irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) (Arami et al. 2005; Alley 2005; Woodard 2001; Benefield et al. 1982; Sivaraj et al. 2001). The values for the adsorption of AR-14 on PSMA are shown in (Table 1).

4 Kinetic Studies

The transient behavior of the dye adsorption process was analysed using pseudo-first-order, pseudo-second-order kinetic models. The linear form of the pseudo-first-order equation is given by the following:

$$\log(q_e - q) = \log q_e - \frac{K_1 t}{2.303}. \quad (8)$$

Table 1 Freundlich and langmuir constants for the removal of AR 114 by PSMA

Langmuir				
q_{max} (mg/g)	K_L (L/mg)	R_L	R	R^2
5.118	1.367	0.057	0.997	0.993
Freundlich				
K_F (mg/g)	n	R	R^2	
2.742	1.935	0.978	0.957	

The linear form of the pseudo-second-order model (Liu 2008) is given as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e}, \quad (9)$$

where q_t are the amounts of dye adsorbed on adsorbent at various time t (mg/g); k_1 is the equilibrium rate constant of pseudo-first order kinetics (min^{-1}), and t is the contact time (min); k_2 is the equilibrium rate constant of the pseudo-second-order kinetics ($\text{g}/(\text{mg min})$); The rate constants predicted equilibrium uptakes and the corresponding correlation coefficients for the adsorbent are summarized. The pseudo-first-order kinetics fits well for the first 30 min, and thereafter, the data deviated greatly from linearity. Thus, the model represents the initial stages where rapid adsorption occurs, but it cannot be applied for the entire adsorption process (Poost et al. 1978). Therefore, the pseudo-first-order model was inapplicable to this system. The correlation coefficients and the q_e cal values from the pseudo-second-order kinetic model are in good agreement with the experimental results.

Figure 8 shows the fitting results using various kinetic models for the adsorbent used for removing AR-14. The pseudo-second-order model provides the best correlation for all the adsorption processes. This suggests that the adsorption systems studied belong to the pseudo-second-order kinetic model, based on the assumption that the rate limiting step may be chemisorption involving electrostatic forces through sharing or exchange of electrons between the adsorbent and the adsorbate.

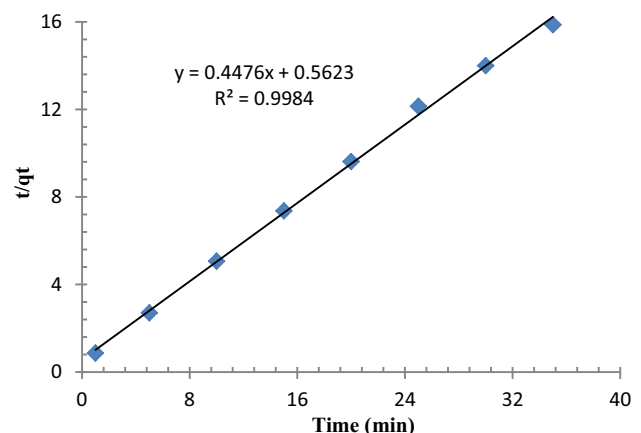


Fig. 8 Relationship of t/q_t versus time to verify pseudo-second-order kinetic equation

5 Conclusion

The results of this study show that the PSMA have suitable adsorption capacity with regard to the removal of AR-14 from its aqueous solution. An initial pH of 6.1 was found to be optimum for maximum AR-14 removal by PSMA. PSMA is easily available material and can be inexpensive alternatives for more costly adsorbents for acid dye removal in wastewater treatment. Adsorption followed both Langmuir and Freundlich isotherms. Adsorption kinetics was found to follow pseudo-second-order rate expression. The study confirms that PSMA can be used as an alternative for more costly adsorbents used for dye removal in wastewater treatment processes.

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