ORIGINAL ARTICLE

Cumulative effect of hydrophobic PLMA and surface epoxide groups in composite polymer particles on adsorption behavior of congo red and direct red-75

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Abstract Industrial application of hydrophobic materials is numerous particularly as adsorption beads to remove organic pollutants. In this research combined effect of hydrophobicity and reactive epoxide group on the adsorption behavior of dye molecules by composite polymer particles was investigated. Lauryl methacrylate (LMA) a poor water soluble long chain vinyl monomer is commercially available. Polystyrene/poly(LMA-divinyl benzene) or PS/P(LMA-DVB) composite seed particles were first prepared by slightly modified activated swelling of micron-sized PS seed particles utilizing either water or water-ethanol dispersion medium. The influence of poly(vinyl alcohol) (PVA) as steric stabilizer on the size and size distribution was evaluated. The poor solubility of LMA in the continuous phase hindered the homogeneous swelling of PS particles even in the presence of ethanol (5% w/w) and resulted in fairly polydispersed PS/P(LMA-DVB) composite seed particles. The composite seed particles were then functionalized with epoxide group by seeded polymerization of glycidyl methacrylate (GMA) to produce PS/P(LMA-DVB)/PGMA composite polymer particles. The epoxide functionalized PS/P(LMA-DVB)/PGMA composite polymer particles were used to adsorb two kinds of azo dyes, congo red (CR) and direct red-75 (DR-75). The effects of initial dye concentration at 303 and 323 K on adsorption behavior were investigated and the adsorption was explained by adsorption isotherms. Temperature dependent adsorption measurements were also carried out at identical initial dye concentration. The adsorption results showed

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that inclusion of reactive epoxide group on/near the surface of hydrophobic PS/P(LMA-DVB) composite seed particles improved the adsorption capacity of dye molecules.

1. Introduction

Micrometer-sized polymer particles are useful in industrial applications such as separation media, resins for ion-exchangers, support materials, toners, coatings, calibration standards, and functional beads for medical diagnostics (Song and Winnik, 2005; Zhou et al., 2007). In some of these applications a certain degree of hydrophobicity is required in order to limit water penetration into polymer particles or specifically to adsorb hydrophobic contaminants. Prominent applications of hydrophobic polymer dispersions include water purification, oil absorbers, viscosity modifiers, resins for chromatography, hydrophobic coatings and oil-soluble drag reducers (Xu et al., 2003, 2007; Meng et al., 2015; Novio and Ruiz-Molina, 2014; Shao et al., 2010). Lauryl methacrylate (LMA) bearing long chain alkyl group could be an ideal monomer to produce hydrophobic polymer particles. But the very poor water solubility ($\ll 0.01$ g/100 g at 25 °C) of LMA made it difficult to polymerize by conventional emulsion polymerization and often resulted in poor conversion with high coagulum formation (Zhou et al., 2007; Yildiz et al., 2003). Even miniemulsion polymerization of LMA is quite challenging and requires special attention to overcome specific instabilities of the monomer droplets (Raghunadh et al., 2004). Few researchers described the homopolymerization and/or copolymerization of LMA in homogeneous conditions employing organic solvents to avoid the problems associated with the hydrophobicity of LMA (Xu et al., 2003; Demetriou and Krasia-Christoforou, 2008; Qiu et al., 2009; Chatterjee and Mandal, 2006; Beers and Matyjaszewski, 2001; Mishra et al., 2001; Sannigrahi et al., 1997). Recently, we proposed that emulsion copolymerization of LMA is possible in water-ethanol dispersion media using water soluble initiator (Ahmad et al., 2011; Shabnam et al., 2013). The addition of ethanol, a solvent for LMA, in the continuous phase favored the formation of submicrometer-sized copolymer latex particles.

The objective of this contribution was to report the possibility of the preparation of micrometer-sized hydrophobic polymer particles based on LMA monomer. Various techniques are available for the preparation micrometer-sized polymer particles such as dispersion polymerization, suspension polymerization, dynamic and activated swelling methods (Suzuki and Yamakawa, 2012; Skelhon et al., 2014; Zhao and Qiu, 2011; Minami et al., 2003; Ugelstad et al., 1985; Ahmad and Tauer, 2003; Okubo et al., 1999). In a previous study we reported the preparation of hydrophobic PLMA latex particles via suspension polymerization in the presence of poly(vinyl alcohol) (PVA) as steric stabilizer (Ahmad et al., 2013). But this process led to quite a high amount of coagulum and PLMA latex particles could not be used for further application studies because of the low glass transition temperature (~ -65 °C) (Peyser, 1989). In a recent study we successfully carried out a kind of combined suspension-precipitation polymerization of the hydrophobic divinyl benzene (DVB)/LMA monomer mixture where monomer droplets contain additional organic liquids (toluene, T, hexadecane, HD, and a 1: 4 mixture T: HD) using oil soluble initiator (Shabnam et al., 2015). The nature of additional solvents and their interactions with co(polymers) determined the internal morphology of P(LMA-DVB) particles.

Here we report the usefulness of activated swelling method for the preparation of epoxide bearing several micrometer-sized cross-linked hydrophobic polymer particles utilizing the hydrophobic nature of LMA and DVB. For this, polystyrene (PS) seed particles were first prepared by dispersion polymerization. Then PS/P(LMA-DVB) compos-

ite seed particles were prepared by seeded copolymerization followed by slightly modified activated swelling of PS seed particles where PS to (LMA + DVB) weight ratio was fixed at 1/200. Finally surface epoxide group was introduced by second step seeded polymerization of glycidyl methacrylate (GMA) in the presence of PS/P(LMA-DVB) composite seed particles. The preparation scheme of epoxide functional PS/P(LMA-DVB)/PGMA composite polymer particles is detailed in Fig. 1. In order to evaluate the applicability of epoxide functional PS/P(LMA-DVB)/PGMA composite polymer particles as adsorbent for the treatment of dye solution a comparative adsorption measurement of two different poor water soluble azo dyes, cong red (CR) and direct red-75 (DR-75) was carried out on both reference PS/P(LMA-DVB) composite seed and PS/P(LMA-DVB)/PGMA composite polymer particles.

2. Experimental details

2.1. Materials and instruments

Styrene (Sigma-Aldrich, USA) was distilled under reduced pressure to remove inhibitor and preserved in the refrigerator. LMA (Fluka Chemika, Switzerland) was purified by passing through activated basic Al_2O_3 followed by treatment with 10% NaOH aqueous solution. Cross-linking agent DVB, 80% grade (Sigma-Aldrich, USA) was used after washing with aqueous 10% NaOH solution and subsequent dehydration with anhydrous $CaCl_2$. GMA (Fluka Chemika, Switzerland) and hexadecane (HD) from Sigma-Aldrich, USA, were used without any purification. Poly(vinyl pyrrolidone) or PVP (Fluka Chemika, Switzerland) of molecular weight 3.6×10^5 g mol^{-1} and poly(vinyl alcohol) or PVA (Thomas Baker Limited, India) of molecular weight 1.4×10^4 g mol^{-1} were used as polymeric stabilizers. 2,2-azobisisobutyronitrile (AIBN) from Fluka Chemika, Switzerland, benzoyl peroxide (BPO) from BDH Chemicals Ltd., UK, and 2,2′-azobis(2-amidinopropane) hydrochloride (V-50) from LOBA Chem., India, were recrystallized from methanol before use. Cationic Sodium dodecyl sulfate, SDS (Fluka BioChemika, Switzerland), aliquate^{336} (tri caprylylmethylammoniumchloride) a quaternary ammonium salt (Fluka Chemika, Switzerland), potassium nitrosodisulfonate or Fremy's salt (Sigma-Aldrich, USA), CR (Matheson Colman & Bell, USA), DR-75 of purity 30% (Sigma-Aldrich, USA) and other chemicals used were of reagent grade. Only the pH range of CR was made available by the supplier. Ethanol was dehydrated by treating with active CaO followed by distillation. Deionized water was distilled using a glass (Pyrex) distillation apparatus.

The particle size distribution was measured by scanning electron microscope, SEM (JEOL, Tokyo, Japan) at a voltage of 20 kV. Fourier transform infrared (FTIR) spectra were recorded for washed polymer samples with a FTIR 8044, Shimadzu, Japan to see the structural composition. Homogenizer (T 18 Digital Ultra Turrax, IKA, Germany) was used to form minidroplets.
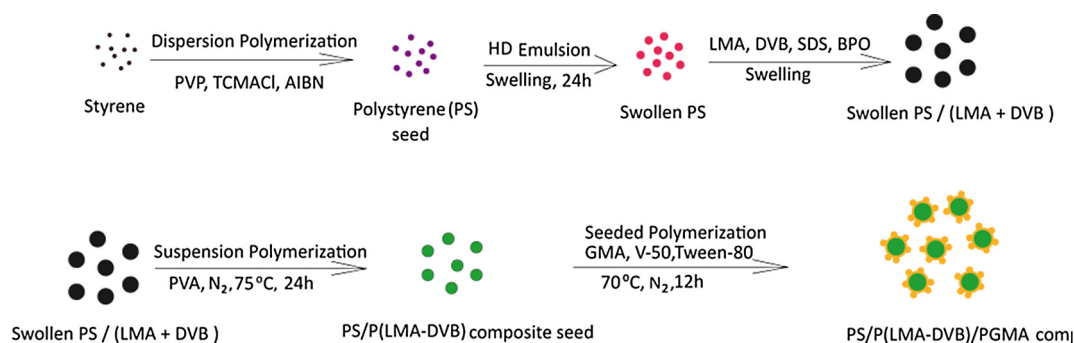
Figure 1 Preparation scheme of PS/P(LMA-DVB)/GMA composite polymer particles.

2.2. Preparation of polystyrene (PS) seed particles by dispersion polymerization

PS seed particles were prepared in a three-necked round bottomed flask equipped with a mechanical stirrer and a reflux condenser. A mixture of 20 g of styrene, 0.8 g of PVP and 0.228 g of aliquate[336] was taken into the reaction flask containing 100 g of ethanol and 5 g of water. Temperature was increased to 70 °C and AIBN (0.2 g) was added to start the polymerization. The polymerization reaction was continued for 24 h. PS seed particles were washed several times by replacing the continuous phase with distilled deionized water.

2.3. Preparation of PS/P(LMA-DVB)/PGMA composite polymer particles

The washed micrometer sized PS particles were used as seed to prepare larger PS/P(LMA-DVB) composite particles. For this conventional activated swelling method was used with some minor modifications. PS seed particles were first swollen with HD emulsion and then with relatively larger amount of LMA and DVB monomer emulsion in the presence of oil soluble initiator BPO. The swelling was carried out in water medium. Prior to the polymerization PVA (0.3 g) was added to stabilize the system. Polymerization conditions are detailed in Table 1.

The swelling of HD swollen PS seed particles with monomer emulsion was also carried out under identical conditions in the presence of 5% (w/w) ethanol based on the total dispersion medium. After swelling variable amount of PVA (0.075–0.30 g) was added prior to the polymerization reaction to see the effect on particle size distribution.

PS/P(LMA-DVB) composite particles prepared in the presence of 5% (w/w) ethanol and 0.15 g of PVA were washed several times by replacing the continuous phase using centrifugation technique and then used as seed particles for the next step seeded polymerization with GMA. For 2 g of PS/P(LMA-DVB) composite particles 1 g of GMA was taken in a three necked round bottomed flask dipped in a thermostat water bath set at 70 °C. Distilled water (56 g) was used as the dispersion medium and seeded polymerization was initiated by cationic V-50 (0.02 g) initiator. This seeded polymerization was continued for 12 h under a nitrogen atmosphere. PS/P(LMA-DVB)/GMA composite polymer particles thus prepared were washed by replacing the continuous phase with fresh distilled water following centrifugation prior to characterization and adsorption study.

Table 1 Preparation of PS/P(LMA-DVB) composite seed particles by activated swelling method.

Ingredients	(g)
PS/LMA + DVB/ (w/w)	1/200
HD emulsion[a]	
HD	0.08
SDS	0.025
Water	12.0
Seed emulsion	
PS particles	0.04
SDS	0.05
Water	25.0
Monomer emulsion[b]	
LMA	7.2
DVB	0.8
SDS	0.075
BPO	0.12
Water	30.0

[a] HD emulsion was prepared by magnetic stirrer, 1000 rpm, 1 h, and then ultrasonically homogenized, 20,000 rpm for 2 min at ice cold temperature. CD and seed emulsions were mixed and stirred at 200 rpm for 24 h at 35 °C. 0.25 g of SDS dissolving in 100 mL of water was added collectively to stabilize the system.

[b] Monomer emulsion was prepared by magnetic stirrer, 900 rpm, 1 h, and then ultrasonically homogenized, 20,000 rpm for 8 min, at ice cold temperature. PS seeds swollen with HD were then mixed with monomer emulsion, stirred at 200 rpm for 24 h at 30 °C, 0.3 g of PVA dissolving in 30 mL of water was added collectively. 10^{-4} mol/L of Fremy's salt was added before seeded polymerization at 70 °C, N_2, 100 rpm, 24 h.

2.4. Comparative adsorption measurements of dye

A comparative temperature dependent adsorption with variable initial dye concentration on both PS/P(LMA-DVB) and PS/(LMA-DVB)/PGMA composite particles was measured. For each adsorption measurement 0.1 g of either PS/P(LMA-DVB) or PS/(LMA-DVB)/PGMA composite polymer particles was mixed with 10 mL aqueous solution containing variable amount of dye. The mixture was allowed to stand with occasional shaking at 303 and 323 K for 2 h. Then the supernatant was separated by centrifugation followed by filtration through a Whatman filter paper and the concentration of dye in the supernatant was measured by UV-visible spectrophotometer at the respective wavelength maxima (CR: 502 nm, DR-75: 522 nm) i.e. the wavelength corresponding

to the maximum absorbance. The amount of adsorbed dye was measured by subtracting the concentration in the supernatant from the initial concentration. Calibration curve of each individual dye was used for this calculation. The adsorption of dyes was quantified using following relations (Postai et al., 2016),

$$q_e = \frac{(C_0 - C_e)v}{w} \qquad (1)$$

where q_e, C_0, C_e, v and W are the equilibrium adsorption capacity (mg g^{-1}), initial dye concentration (mg L^{-1}), dye concentration at time t (mg L^{-1}), volume of the solution (L) and weight of the particles (g).

Temperature dependent adsorption measurements on both PS/P(LMA-DVB) composite seed and PS/(LMA-DVB)/PGMA composite polymer particles were also carried out at four different temperatures (303, 313, 323 and 333 K). For this 0.1 g of each composite particles was mixed with 10 mL aqueous solution containing 0.15 mg of dye and the dye-particle mixture was allowed to stand for 2 h with occasional shaking at the respective temperature. The amount of adsorption was measured under identical condition as stated above.

Most organic dyes are sensitive to changes in pH value. CR is a dipolar molecule, and exists as anionic form at basic pH (> 5.5) and as cationic form at acidic pH (< 5.5). On the other hand our prepared PS/P(LMA-DVB)/PGMA composite polymer particles are partially positively charged due to the use of cationic V-50 initiator during seeded polymerization. So it is obvious that a variation in pH would influence the adsorption amount due to electrostatic interaction with charged particles. To avoid repulsion between like charges of CR molecules at pH < 5.5 (acidic) and particle surface, pH ~ 6 was considered as better choice for adsorption measurements of CR. On the contrary DR-75 a similar kind of dye as DR-80 is expected to show no considerable change in adsorption behavior with pH variation (Ardejani et al., 2008). So overall to have a better comparison and better control over the experimental conditions pH ~ 6 was selected for all adsorption experiments.

2.5. Adsorption isotherms

To study the adsorption performance of dye molecules on PS/P(LMA-DVB) and PS/(LMA-DVB)/PGMA composite polymer particles several isotherms such as Langmuir, Freundlich, and Temkin adsorption isotherms were used to analyze the experimental data. The Langmuir adsorption isotherm (Langmuir, 1916; Wong et al., 2003; Ho et al., 2002; Hu et al., 2011) assumes the saturated monolayer adsorption of the adsorbent onto the adsorbate and is given by

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L C_e} \qquad (2)$$

where q_e and C_e have the same meanings as noted early, q_m is the monolayer saturation adsorption capacity of adsorbate (mg/g), K_L is characteristic adsorption constant (L/mg). The Freundlich adsorption isotherm (Freundlich, 1906; Ozcan and Ozcan, 2005; Sadeghi-Kiakhani et al., 2013) represents the multilayer physisorption can be expressed as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (3)$$

where K_F and n are the characteristic constants.

Also isotherm data were tested with the Temkin adsorption isotherm (Temkin, 1941) which indicates the chemisorption mechanism of adsorption phenomenon that can be expressed as

$$q_e = a + b \log c_e \qquad (4)$$

where a and b are the constants, the adsorbent-adsorbate relative affinity in the adsorption process.

3. Results and discussion

3.1. Latex characterization

SEM photographs of PS seed and PS/P(LMA-DVB) composite seed particles are illustrated in Fig. 2. The latter was prepared by modified activated swelling method with swelling carried out in water medium followed by seeded copolymerization in the presence of PVA. The average diameters and coefficient of variations of (CVs) of PS seed and PS/P(LMA-DVB) composite seed particles are 0.92 μm, 23.26% and 2.44 μm, and 57.8% respectively. It is evident that both seed and composite seed particles are bit polydispersed and the polydispersity index increases after activated swelling followed by seeded polymerization. The size distribution of PS/P(LMA-DVB) composite seed particles ranged between 1.14 and 5.25 μm, larger than the average size of PS seed particles. For the preparation of PS/P(LMA-DVB) composite seed particles the swelling of HD swollen PS seed particles was carried out in the presence of monomer droplets dispersed in aqueous phase. The matter of fact is that swelling of PS seed particles cannot proceed smoothly if the solubility of monomer(s) in the continuous phase is below a certain threshold. Because this event requires the diffusion of monomer from monomer droplets through the aqueous phase to the HD swollen PS seed particles. This has earlier been demonstrated for emulsion polymerization of extremely hydrophobic LMA (Ahmad et al., 2011; Shabnam et al., 2013). To overcome the diffusional hindrance the presence of 5% (w/w) ethanol in the continuous phase was studied during swelling of PS seed particles in the presence of monomer droplets. Fig. 3 shows the SEM photographs of PS/P(LMA-DVB) composite seed particles prepared in the presence of various amounts of PVA as steric stabilizer. The average diameters of composite particles are 2.61, 2.95 and 2.53 μm prepared in the presence of 0.075, 0.15, and 0.3 g PVA respectively. The polydispersity index is pretty high in all three cases with a minimum (46%) is observed for composite particles prepared in the presence of 0.15 g PVA. From the above result it can be concluded that addition of ethanol did not favor the smooth homogeneous swelling of PS seed particles with hydrophobic monomer (LMA-DVB) mixture despite the improvement of solubility in the continuous phase. The PS/P(LMA-DVB) composite seed particles prepared in the presence of 0.15 g PVA were used for surface modification with epoxide functionality via seeded polymerization in the presence of GMA. The average size and CV of washed PS/P(LMA-DVB)/PGMA composite polymer particles measured from SEM photograph (Fig. 4) are 4.28 μm and 45.3%. The multiple protrusions on PS/P(LMA-DVB)/PGMA composite polymer particles are possibly owing to the phase separation occurred during swelling of seed particles with monomer. The higher crosslinking density in PS/
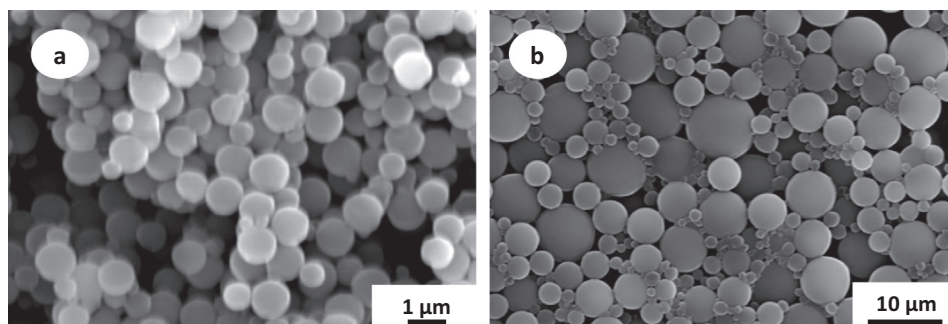
Figure 2 SEM images of (a) PS seed and (b) PS/P(LMA-DVB) composite seed particles prepared by (a) dispersion polymerization and (b) activated swelling of PS seed in water followed by seeded polymerization (b).
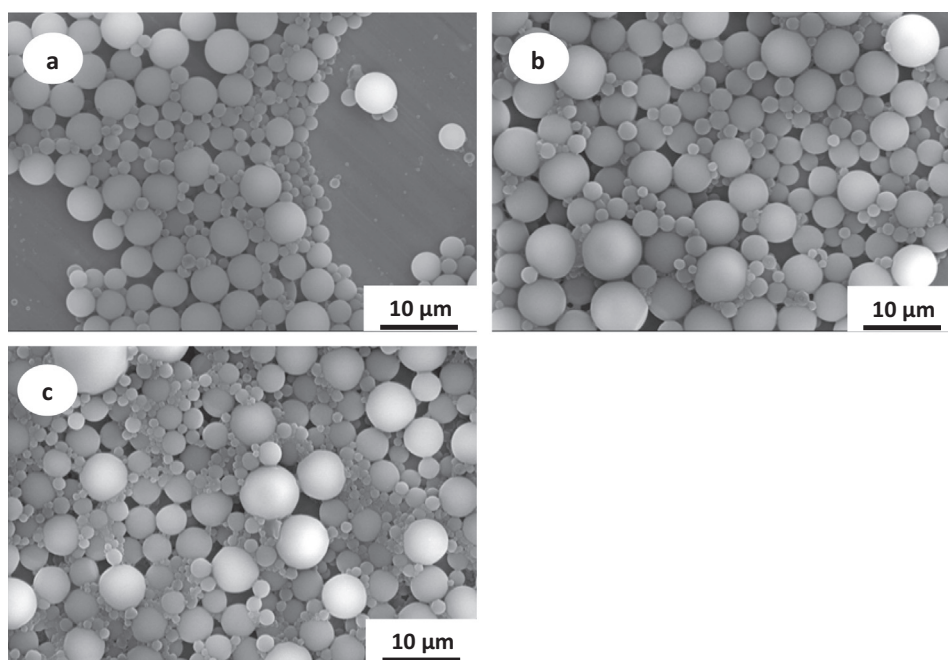

Figure 3 SEM images of PS/P(LMA-DVB) composite seed particles prepared by activated swelling of PS seed in 5% ethanol containing aqueous media having PVA (g): (a) 0.075, (b) 0.15, and (c) 0.3.

P(LMA-DVB) composite seed particles generally favors the formation of protruded surface structure (Kraft et al., 2011; Kim et al., 2009; Ahmad et al., 2007). The increase in average size and change in morphology following seeded polymerization confirm the formation of PS/P(LMA-DVB)/PGMA composite polymer particles.

FTIR spectral analysis of polymer particles gives idea about the structural composition of the surface. A comparative plot of PS seed, PS/P(LMA-DVB) and PS/P(LMA-DVB)/PGMA composite particles is shown in Fig. 5. In the spectrum of PS seed particles the absorption signals in the regions 2835–2930 and 3013–3150 cm^{-1} represent the characteristic aliphatic and aromatic ─CH stretching vibrations. Compared to this in PS/P(LMA-DVB) composite seed particles the intensity of aliphatic ─CH stretching vibration becomes stronger while the aromatic ─CH stretching vibration almost disappears. A new absorption signal corresponds to the stretching vibration of ester carbonyl group derived from LMA appears at 1715 cm^{-1}. In the spectrum of PS/P(LMA-DVB)/PGMA com-
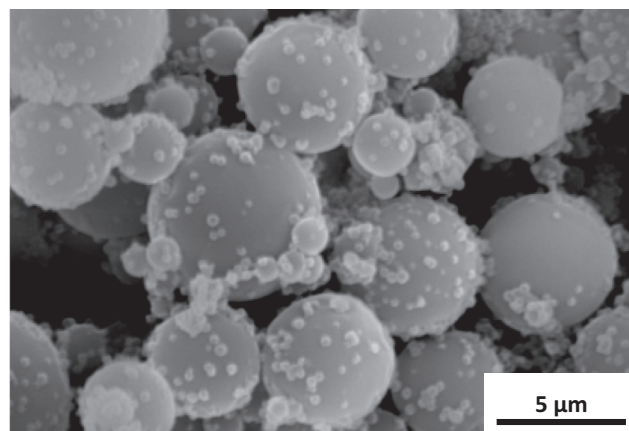

Figure 4 SEM image of PS/P(LMA-DVB)/PGMA composite polymer particles prepared by seeded polymerization.
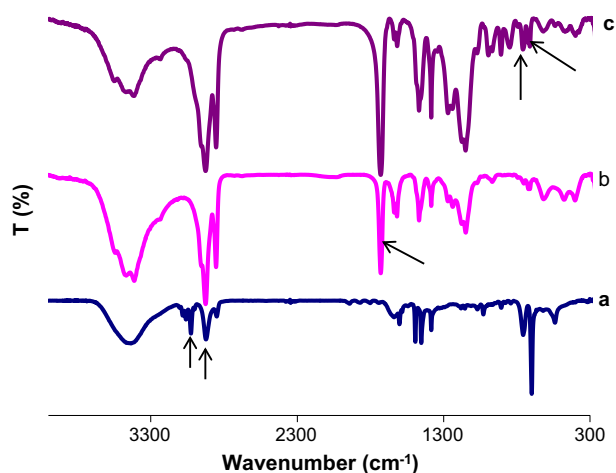
Figure 5 FTIR spectra of (a) PS seed, (b) PS/P(LMA-DVB) composite seed and (c) PS/P(LMA-DVB)/PGMA composite polymer particles recorded in KBr pellets.

posite polymer particles two characteristic absorption bands due to epoxide group appear at 968 and 915 cm^{-1} respectively. These results suggest that epoxide group is located on/near the surface of PS/P(LMA-DVB)/PGMA composite polymer particles.

3.2. Adsorption capacity

Industries such as textile, paper, plastics, paint, tanning, printing ink, cosmetics, use great volume of chemical dye for coloring the manufactured articles and discharge large amount in water stream during industrial processing causing serious environmental problems due to their negative ecotoxicological
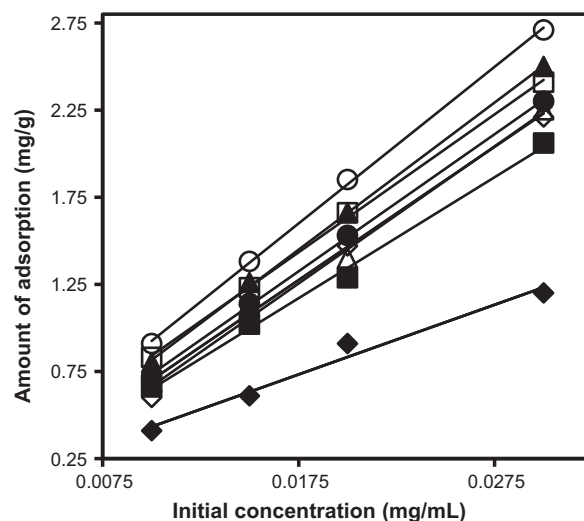

Figure 7 Concentration dependent adsorption behavior of CR ($\blacktriangle$, $\bullet$, $\triangle$, $\circ$) and DR-75 ($\blacklozenge$, $\blacksquare$, $\diamond$, $\square$) on reference PS/P(LMA-DVB) composite seed (closed symbol) and PS/P(LMA-DVB)/PGMA composite polymer particles (open symbol) at 303 K ($\blacklozenge$, $\blacktriangle$, $\diamond$, $\triangle$) and 323 K ($\blacksquare$, $\bullet$, $\square$, $\circ$). pH: 6, Immobilization time: 2 h, polymer solid: 0.1 g.

effects and bioaccumulation in living organisms. According to the World Bank estimates about 17–20% of industrial water pollution comes from textile dyeing and treatment (Ahmad et al., 2007). Recently researchers are showing interest in designing new low cost effective adsorbent with high adsorption capacity and strong mechanical properties for dye removal from industrial wastewaters (Bayramoglu et al., 2012; Shukla and Madras, 2012; Li et al., 2013; Kyzas et al., 2010; Mubarekyan and Santore, 1998; Bhattacharyya and Ray, 2013; Bayramoglu and Arica, 2013; Kuringen et al.,
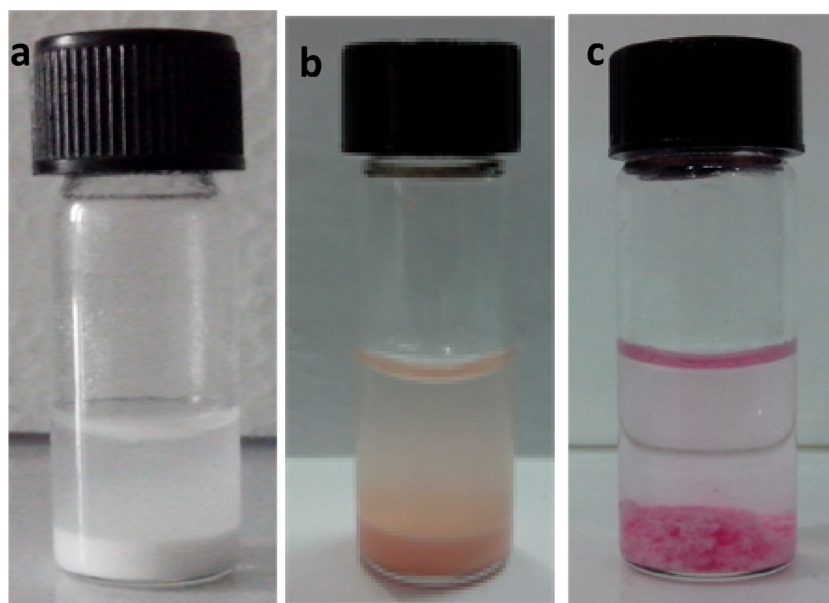

Figure 6 Digital images of PS/P(LMA-DVB)/PGMA composite polymer particles after sedimentation: (a) blank, (b) CR adsorbed and (c) DR-75 adsorbed.
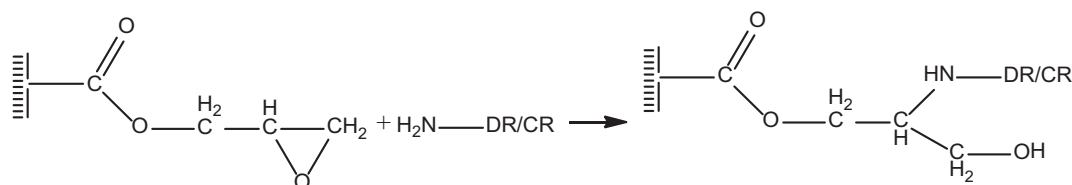
Figure 8   Reaction scheme among amine groups of dye molecules and epoxide groups of PGMA.
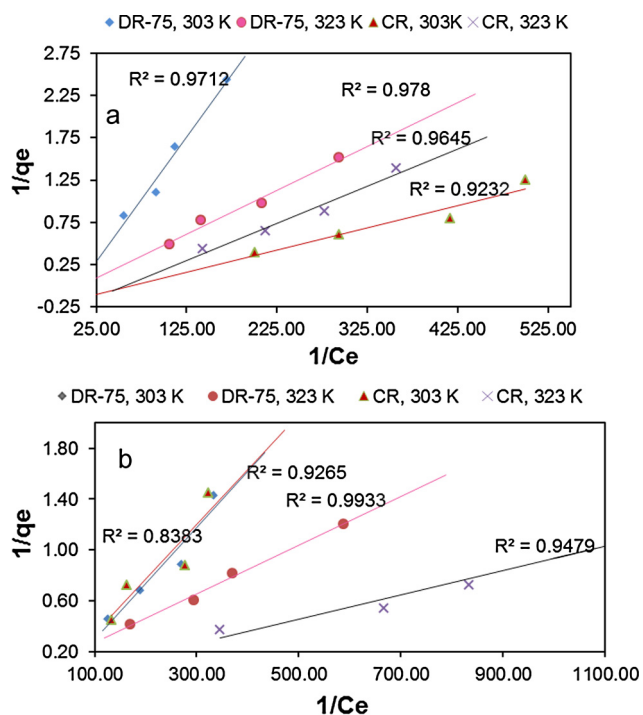

Figure 9   Langmuir adsorption isotherms for CR and DR-75 adsorption on (a) PS/P(LMA-DVB) composite seed and (b) PS/P (LMA-DVB)/PGMA composite polymer particles.

Figure 10   Freundlich adsorption isotherms for CR and DR-75 adsorption on (a) PS/P(LMA-DVB) composite seed and (b) PS/P (LMA-DVB)/PGMA composite polymer particles.

2014; Kumar and Tamilarasan, 2013). The potential of epoxide modified PS/P(LMA-DVB)/PGMA composite polymer particles as adsorbent for removal of two model azo dyes (CR, DR-75) was examined and the results are compared with reference PS/P(LMA-DVB) composite seed particles. So the following research has been focused mainly on the adsorption behavior and adsorption capacity of polymer particles rather than on adsorption kinetics. In order to find the optimum adsorption time a series of experiment was performed at an initial dye (CR and DR-75) content of 0.15 mg taken in 10 g distilled water containing 0.1 g polymer adsorbent. The adsorption of dye increased with time and reached equilibrium after 2 h of mixing (data not shown) and did not increase further. PS/P(LMA-DVB)/PGMA composite polymer particles became colored by adsorbing dye from aqueous solution leaving a light colored dye solution as shown in Fig. 6. The effect of initial dye concentration on the equilibrium adsorption capacity of PS/P(LMA-DVB) composite seed and PS/P (LMA-DVB)/PGMA composite polymer particles for CR and DR-75 dyes is shown in Fig. 7. The adsorption capacity increases with the increase in initial dye concentration. The higher concentration of dye reduces the surface tension and
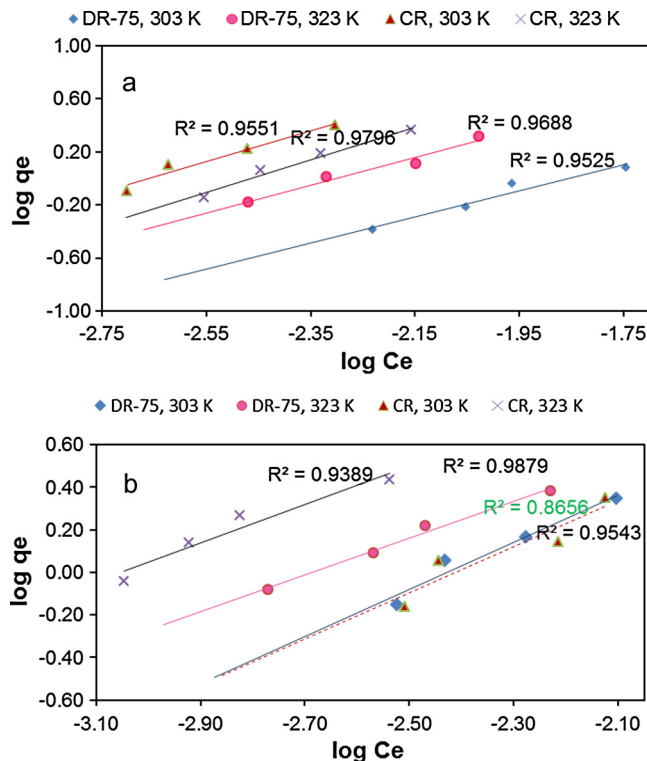
similarly the free (surface) energy of the system. The extent of adsorption therefore increases due to such decreasing tendency of the free energy. The adsorption capacity of specific dye on the surface of epoxide functional PS/P(LMA-DVB)/ PGMA composite polymer particles is partially higher than that on reference PS/P(LMA-DVB) composite seed particles. It is to be mentioned that total surface area of PS/P(LMA-DVB)/PGMA composite polymer particles is lower than that of reference PS/P(LMA-DVB) composite seed particles as the former has larger particle size distribution. So the trend in adsorption pattern based on per unit mass of particles as presented in Fig. 7 would be same even if the data are presented in mass per unit area of particles. For information, based on surface area the adsorption capacity on PS/P (LMA-DVB)/PGMA composite polymer particles is at least 1.5 times higher than on reference composite seed particles. However, the calculation based on mass per unit area has been avoided due to high polydispersity index. The increase in adsorption capacity attributes to the formation of covalent
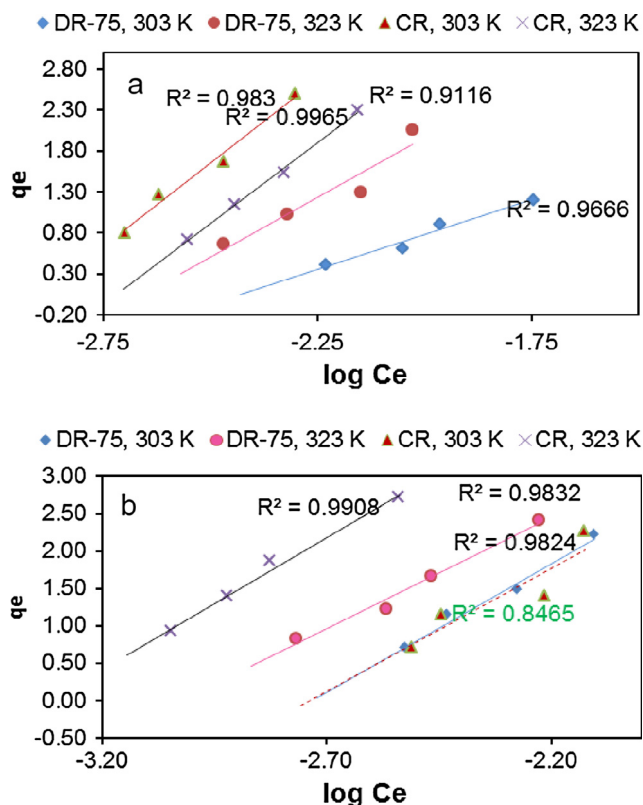
● DR-75, 303 K ● DR-75, 323 K ▲ CR, 303 K × CR, 323 K

● DR-75, 303 K ● DR-75, 323 K ▲ CR, 303 K × CR, 323 K

Figure 11 Temkin adsorption isotherms for CR and DR-75 adsorption on (a) PS/P(LMA-DVB) composite seed and (b) PS/P(LMA-DVB)/PGMA composite polymer particles.

linkage between $-NH_2$ groups of dye molecules and epoxide groups (Fig. 8) on the particle surface (Wang et al., 2006; Alam et al., 2012). Temperature effect on the comparative adsorption capacity is also evident with the variation of nature of dye molecules. The amount of adsorption is higher at higher temperature except for CR on PS/P(LMA-DVB) composite seed particles. To understand such variation a detail study on equilibrium data isotherm has been made in the following paragraphs.
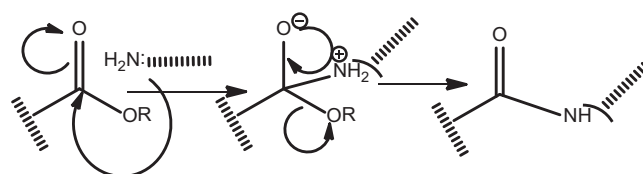

Figure 12 Scheme of chemical reaction between ester groups of PS/P(LMA-DVB) composite seed particles and amine groups of dye molecules.

The equilibrium data isotherm analyses for CR and DR-75 adsorption on both reference PS/P(LMA-DVB) composite seed and epoxide functional PS/P(LMA-DVB)/PGMA composite polymer particles at temperatures 303 and 323 K are shown in Figs. 9–11. The equilibrium data have been analyzed by linear regression of isotherm model equations, such as Langmuir (Fig. 9a and b), Freundlich (Fig. 10a and b) and Temkin (Fig. 11a and b). The related empirical constants obtained by calculation from the values of slopes and intercepts of the respective linear plots are shown in Table 2. The data indicate that the adsorption of CR and DR-75 on PS/P (LMA-DVB)/PGMA composite polymer particles at 303 K fits well with Freundlich and Temkin adsorption isotherms respectively. This indicates that adsorption of CR and DR-75 follows multilayer physisorption and chemisorption respectively. At higher temperature of 323 K, Temkin and Langmuir adsorption isotherms are the most appropriate to describe the adsorptions of CR and DR-75 on PS/P(LMA-DVB)/PGMA composite polymer particles i.e. they follow chemisorption and monolayer physisorption respectively. Conversely, independent of temperature the adsorptions of CR and DR-75 on reference PS/P(LMA-DVB) composite seed particles follow identical Temkin and Langmuir adsorption models, i.e. chemisorption and monolayer physisorption respectively. The adsorption process is a complex phenomenon depending on many factors that might influence the adsorption behavior; these include the dye structure and size, adsorbent surface properties, hydrogen bonding, van der Waals forces, covalent interaction and electrostatic force. Both CR and DR-75 are azo dyes containing amine groups in their structure. PS/P

Table 2 Empirical constants for the DR-75 and CR adsorption on PS/P(LMA-DVB) composite seed and PS/P(LMA-DVB)/PGMA composite polymer particles.

| Temperature	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
	K_L (L mg^{-1})	Q_m (mg g^{-1})	R	n	K_F (L mg^{-1})	R	a	b	R
PS/P(LMA-DVB): DR-75									
303 K	0.071	14.49	0.985	1.01	0.068	0.976	1.69	4.16	0.983
323 K	0.200	31.25	0.989	0.95	0.258	0.984	2.93	7.83	0.954
PS/P(LMA-DVB): CR									
303 K	0.500	5.95	0.961	0.87	1.183	0.977	4.07	11.82	0.991
323 K	0.250	4.03	0.982	0.81	1.104	0.989	3.94	10.76	0.998
PS/P(LMA-DVB)/PGMA: DR-75									
303 K	0.250	6.45	0.962	0.90	0.485	0.977	3.43	9.37	0.991
323 K	1.000	13.33	0.996	1.15	0.215	0.993	2.98	9.02	0.991
PS/P(LMA-DVB)/PGMA: CR									
303 K	0.250	10.87	0.915	0.92	0.410	0.930	3.30	9.04	0.920
323 K	1.000	52.63	0.973	1.11	0.552	0.969	3.53	11.72	0.995
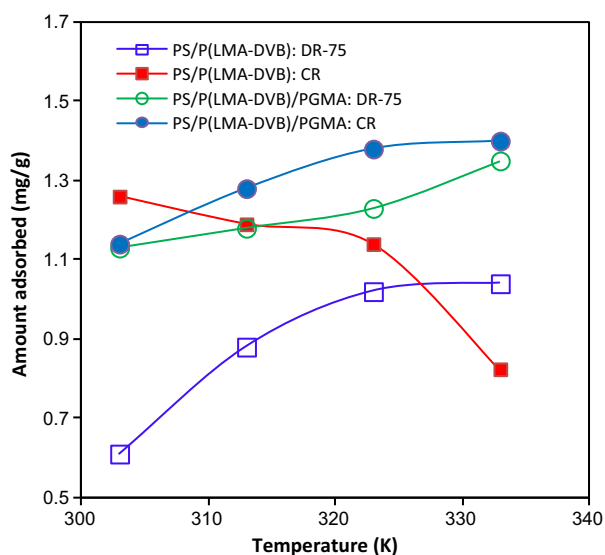
Figure 13 Temperature dependent adsorption behavior of CR and DR-75 on PS//P(LMA-DVB) composite seed and PS/P (LMA-DVB)/PGMA composite polymer particles. pH: ∼6, Immobilization time: 2 h, dye: 0.15 mg, polymer solid: 0.1 g.

(LMA-DVB) composite seed particles and corresponding epoxide functional composite polymer particles possess different surface properties with the later having reactive group on/near the surface. The complexation between dye molecules and PS/P(LMA-DVB)/PGMA composite polymer particles is expected to take place via the van der Waals forces (weak interaction) and hydrogen- and covalent-bonding (strong interaction). Conversely in case of reference seed particles complexation is expected to occur via vander Waals and hydrogen bonding interaction. According to some literature chemical reaction between ester group of PS/P(LMA-DVB) composite seed particles and amino group of dye molecules may also take place as shown in Fig. 12 (Clayden et al., 2012). The adsorption isotherms tell us that such chemical reaction may have occurred only for low molecular weight CR.

A comparison of maximum adsorption capacity (q_m) obtained from Langmuir adsorption isotherms shows different adsorption behaviors for CR and DR-75 on PS/P(LMA-DVB) composite seed and PS/P(LMA-DVB)/PGMA composite polymer particles. The adsorption capacity of PS/P(LMA-DVB) composite seed particles for CR is lower (5.95 mg/g at 303 K and 4.03 mg/g at 323 K) than that of PS/P(LMA-DVB)/PGMA composite polymer particles (10.87 mg/g at 303 K and 52.63 mg/g at 323 K). Contrary to this the adsorption capacity of PS/P(LMA-DVB) composite seed particles for DR-75 is higher (14.49 mg/g at 303 K and 31.25 mg/g at 323 K) than that of PS/P(LMA-DVB)/PGMA composite polymer particles (6.45 mg/g at 303 K and 13.3 mg/g at 323 K). Hence the maximum adsorption capacity of dye molecules on PS/P(LMA-DVB) composite seed particles follows the order: DR-75 > CR i.e. increases with increasing molecular weight. Compared to this on PS/P(LMA-DVB)/PGMA composite polymer particles the maximum adsorption capacity of dye molecules follows reverse order i.e. decreases with increasing molecular weight. The epoxide functionality on/near the surface of composite particles is expected to favor chemisorption to certain extent. As the molecular weight of the dye molecule increases, the access of larger dye molecule becomes relatively difficult to the reactive epoxide groups of the adsorbent. On the contrary the adsorption process of specifically DR-75 on PS/P(LMA-DVB) composite seed particles is probably dominated by physisorption due to hydrophobic interaction whereas CR may undergo some sort of chemical reaction as predicted above.

The effect of temperature on the equilibrium amount of adsorption (q_e) of CR and DR-75 on seed and corresponding epoxide functional composite polymer particles is illustrated in Fig. 13. The amount of adsorption of CR and DR-75 increases with the increase in temperature on PS/P(LMA-DVB)/PGMA composite polymer particles. The rate of increase in amount of adsorption is dependent on the molecular weight as the low molecular weight CR reaches maximum value at relatively lower temperature. Both physi- and chemisorption contributed to adsorption amount on epoxide functional composite particles. Compared to this, on reference PS/P(LMA-DVB) com-
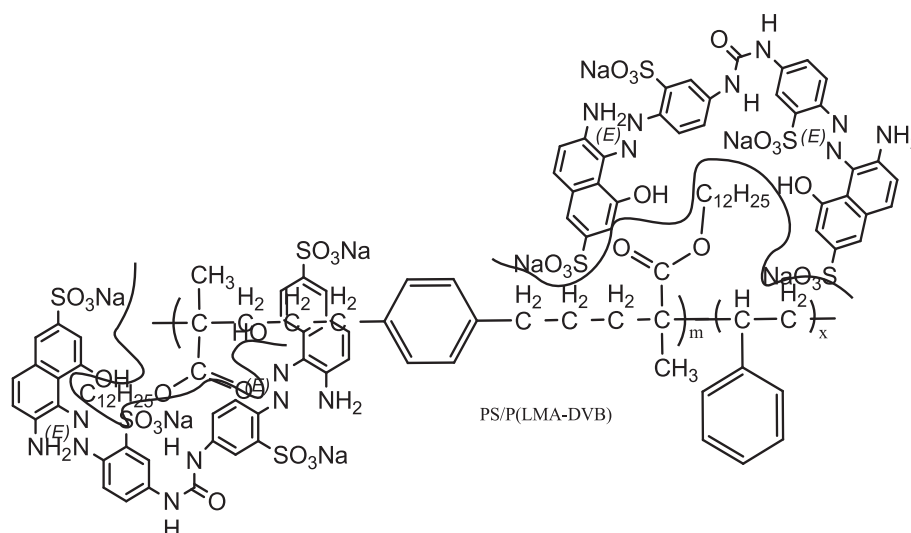

Figure 14 Structural confliction during adsorption of DR-75 on PS//P(LMA-DVB) composite seed particles.

posite seed particles only physisorption is expected to be preferred. Fig. 13 indicates that the amount of adsorption of DR-75 on reference seed particles increases with temperature while that of CR decreases. The decrease in CR adsorption at higher temperature can be explained by considering the simultaneous desorption of physically adsorbed one at higher temperature stimulated by thermal agitation or increase in entropy. Comparatively high molecular weight DR-75 may have contributed to stronger adsorption due to increased non-polar character and thereby reduced the degree of desorption. Structural conflict during adsorption for high molecular weight DR-75 may also retard the desorption once they are physically adsorbed on PS/P(LMA-DVB) composite seed particles as illustrated in Fig. 14.

4. Conclusion

PS/P(LMA-DVB) composite seed particles were prepared by modified activated swelling of micrometer-sized PS seed particles with large amount of hydrophobic LMA-DVB monomer mixture. The obtained particles were polydispersed and the dispersity index was almost independent of the composition of continuous phase and PVA content. Epoxide functional PS/P(LMA-DVB)/PGMA composite polymer particles were prepared by seeded polymerization of GMA in the presence of composite seed particles. FTIR study revealed that epoxide groups are localized on/near the PS/P(LMA-DVB)/PGMA composite polymer particle surface. The adsorption properties of two different azo dyes, CR and DR-75 were investigated to determine the application potential of PS/P(LMA-DVB)/PGMA composite polymer particles as adsorbent for dye removal from water. The equilibrium adsorption capacity increased with initial dye concentration on both epoxide functional composite and reference composite seed particles. Relative to composite seed particles the introduction of epoxide reactive group on/near the surface of composite polymer particles improved the adsorption capacity by at least 1.5 times based on total surface area. Adsorption data were evaluated by Langmuir, Freundlich and Temkin adsorption isotherms and the results showed that on PS/P(LMA-DVB)/PGMA composite polymer particles CR and DR-75 adsorption can be best expressed by Freundlich and Temkin models at 303 K and fitted better to Temkin and Langmuir models at 323 K. PS/P(LMA-DVB)/PGMA composite polymer particles possessed good application potential as industrial adsorbent for removal of dye from wastewater.

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