

*Full Length Research Paper*

# Removal of C.I. Basic Red 46 (BR 46) from contaminated water by adsorption onto hardened paste of Portland cement: Equilibrium isotherms and thermodynamic parameters study

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The present study was carried out to investigate the potential of hardened paste of Portland cement (HPPC) as a low-cost adsorbent for the removal of Basic Red 46 (BR 46) from contaminated water by using batch adsorption studies. In this work, HPPC has been selected as adsorbent because of the main advantages such as high efficiency, simple separation of sludge, abundant availability and low-cost material. The removal of dye in aqueous medium through the process of adsorption with HPPC under a set of variables (contact time, adsorbent dosage, pH, temperature and adsorbent particles size) has been investigated. Results showed that removal of BR 46 increased over 80% with increasing adsorbent dosage, temperature, contact time, pH and adsorbent particle size decreasing. Also the equilibrium adsorption data were fitted well for Temkin isotherm. The adsorption of BR 46 was endothermic and spontaneous with  $\Delta H^\circ$  values of  $+5.452 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ$  values of  $0.035 \text{ JK}^{-1} \text{ mol}^{-1}$ . The free energy changes  $\Delta G^\circ$  was evaluated with temperature increasing. From the experimental results, it may be concluded that HPPC was an efficient and economical adsorbent for BR 46 removal.

**Key words:** Adsorption, Basic Red 46 removal, hardened paste of Portland cement, kinetics, equilibrium isotherm, thermodynamic.

## INTRODUCTION

Effluents from the textile industry contain various kinds of synthetic dyestuffs, and there has been increasing scientific interest in regard to decolorization of these effluents in the last few decades (Karadag et al., 2007). Removing color from wastes is often more important than other colorless organic substances, because the presence

sence of small amounts of dyes (below 1 ppm) is clearly visible and influences the water environment considerably (Daneshvar et al., 2003). Many industries, such as plastics, textile, paper and printing use dyes in order to color their products. Most of dye wastes are toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms. The total dye consumption of textile industries worldwide is in excess of  $10^7 \text{ kg/year}$  (Wong et al., 2004). These processes generate considerable amount of wastewater, which may contain strong color, suspended particles, high pH and high chemical oxygen demand (COD) concentration (Daneshvar et al., 2006). If discharged in environment without any treatment, they are highly harmful. Because of the complexity

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**Abbreviations:** HPPC, Hardened paste of Portland cement; SEM, scanning electron microscopy; COD, chemical oxygen demand.

and the variety of dyes employed in the dyeing processes, it is difficult to find a unique treatment that insures complete elimination of all types of dyes (Mounir et al., 2007). In general, the treatment of dye-containing effluents is being undertaken by adsorption, oxidation–ozonation, biological processes, coagulation–flocculation and membrane processes. But adsorption is a promising removal technique that produces effluents containing very low levels of dissolved organic compounds (Chandra et al., 2007) and releases no harmful compounds into water body. So far, different adsorbents such as fly ash and lignite (Iqbal and Ashiq, 2007), sawdust (Garg et al., 2004, 2003; Ozacar and Sengil, 2005), barley husk (Robinson et al., 2002), peat (Ho and McKay, 1998), silica (McKay et al., 1981), activated carbon (Orfao et al., 2006; Jumariah et al., 2005; Gurses et al., 2006) and soya cake (Daneshvar et al., 2002) have been found in literature. In the present study, we have developed a simple, cost effective removal technique using a commercially available Fe-Al-Si-O<sub>2</sub> containing complex material (hardened paste of Portland cement). Portland cement, a low-cost fine-powdered building material usually consists of four main components such as tricalcium silicate, dicalcium silicate, tricalcium aluminate, tetracalcium aluminoferrite. Portland cement was mixed with water to get hydrated cement. The main advantage of using hydrated cement over other chemical treatment methods is that it does not produce sludge, abundant availability and low-cost material (Kundu et al., 2004; Kagne et al., 2008). The aim of the present work is to study the removal of azo dye, Basic Red 46 (Table 1) onto hardened paste of Portland cement, which is found in plenty in market under different conditions.

## MATERIALS AND METHODS

### Materials

Portland cement used for this study was obtained from local commercial sources. Basic Red 46 with a labeled purity of more than 99% was purchased from Bezema (Switzerland). Sodium hydroxide and hydrochloric acid for pH adjusting was purchased from Merck. Dye solution were prepared by dissolving dye in distilled water.

### Preparation of adsorbent

Approximately 500 g of commercially available Portland cement was taken in a pot and the required amount of distilled water was added to it to make a slurry. The pH of HPPC in pure water was about 9. The slurry was then kept for 26 days under ambient condition for hardening/drying. After complete air drying, the hardened solid paste of cement was broken into small granules of 2 - 3 mm size. The granules were kept immersed under water for 1 h and dried in an oven at 100 - 110°C for 4 h and its pH of point of zero charge (PZC) (Mustafa et al., 2002) was determined equal to 2.

### Batch adsorption studies

Experiments were performed using a batch equilibrium technique

by placing 0.5 g of adsorbent in a glass bottle containing 50 ml of a dye solution at various concentrations. The experiments were carried out at different pHs (2, 5, 7, 8 and 10), temperature values (25, 35, 45, 55 and 65°C), adsorbent masses (0.1, 0.5, 1, 1.5 and 2 g), adsorbent particles size and contact times with shaking by Heidolph MR 3001 K magnetid stirrer at 200 rpm. The solution pH was adjusted at desired level with 0.1 M NaOH or HCl solutions using a HACH sens ion3 pH meter. The residual concentration of dye was determined at  $\lambda_{max} = 531$  nm using a UV/Vis spectronic 501(Milton Roy) spectrophotometer. Absorbance versus concentration data for standard BR 46 solutions were treated by linear regression analysis with  $r^2 = 0.998$ . Absorbance data were converted into concentrations using this calibration line. The efficiency of color removal was expressed as the percentage ratio of removed dye concentration to that of initial one (Equation 1). Where  $C_0$  is the initial concentration of BR 46 (mg l<sup>-1</sup>) and  $C$  the concentration of dye at time  $t$  (min):

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

### Determination of adsorption isotherms

The adsorption isotherms of BR46 on HPPC was determined on the basis of batch analysis. Different amounts of HPPC were allowed to equilibrate with 100 ml dye solution of 50 ppm. Because of enough confidence of approach to equilibrium, these solutions were allowed to stay 3 days in experimental condition, then the equilibrium concentration of dye solutions were measured spectrophotometrically. The amount of dye adsorbed per mass unit of HPPC in equilibrium condition,  $q_e$ , was calculated by Equation 2:

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

where  $V$  is the volume of dye solution in L,  $C_0$  and  $C_e$  are the initial and equilibrium concentrations, respectively, of the dye solutions in ppm, and  $m$  is the mass of the HPPC in g.

### SEM analysis

SEM images were taken by VEGA/TESCAN (Czech Republic) before the HPPC was allowed to adsorb the BR 46. The analysis of the images showed the height of heterogeneous pores within HPPC particles where adsorption could occur.

## RESULTS AND DISCUSSION

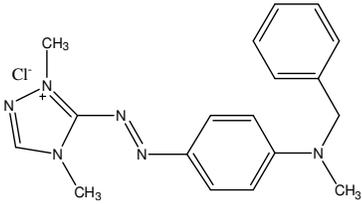
### Effect of contact time

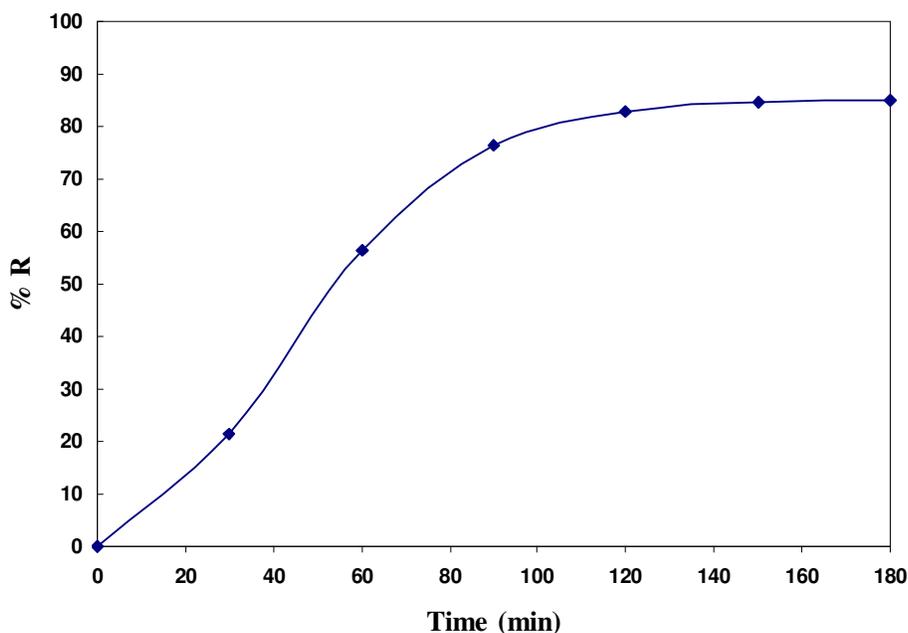
In order to make a comparative study for adsorption of BR 46 in a fixed amount of HPPC ( $m = 0.5$  g), the initial concentration of dye ( $C_0 = 15$  ppm),  $pH_i$  (6.7) and temperature ( $T = 25^\circ\text{C}$ ) were kept the same in all adsorption experiments (Figure 1). It was observed that the amount of dye adsorbed increased with increase in contact time and reached equilibrium after 100 min.

### Effect of adsorbent dosage

The effect of adsorbent dosages on BR 46 uptakes for different amounts of HPPC in the initial concentration of

**Table 1.** Properties of Basic Red 46.

Color index	Basic Red 46
C.I. number	110825
Chemical Name	1H-1,2,4-Triazolium, 1,4-Dimethyl-5-[[4-[methyl(phenylmethyl)amino]phenyl]azo], chloride
Type	Cationic
Azo Groupe	One
Chemical structure	
$\lambda_{\max}$	531 nm
Molecular Formula	$C_{18}N_6H_{21}$
Molecular Weight ( $g\ mol^{-1}$ )	357.5

**Figure 1.** Effect of contact time on removal of BR 46 at:  $C_0 = 15$  ppm,  $pH_i = 6.7$  and  $T = 25^\circ C$ .

dye ( $C_0 = 15$  ppm),  $pH_i$  (6.7) and temperature ( $T = 25^\circ C$ ) is shown in Figure 2. It was observed that the colour removal increases up to a certain limit and then it remains almost constant. Increase in the adsorption with adsorbent dosage can be attributed to increased adsorbent surface area and the availability of more adsorption sites while the number of adsorbate molecules is constant (Shukla et al., 2002).

### Effect of pH

Figure 3 showed the effect of different values of initial

$pH_s$  (2, 5, 7, 8, 10) on the adsorption of BR 46 at constant initial concentration of dyes ( $C_0 = 15$  ppm), 0.5 g of HPPC and temperature ( $T = 25^\circ C$ ). The magnitude of electrostatic charges imparted by ionized dye molecules is primarily controlled by the pH of medium. The amount of dye adsorbed or rate of adsorption tends to vary with pH of aqueous medium. From Figure 3, the dye removal changes shows that the adsorption of the dye increased with pH. Several reasons may be related to the adsorption of dye by the adsorbent relative to pH. The surface of the adsorbent contains large number of reactive sites. At lower pH, the surface of the HPPC gets

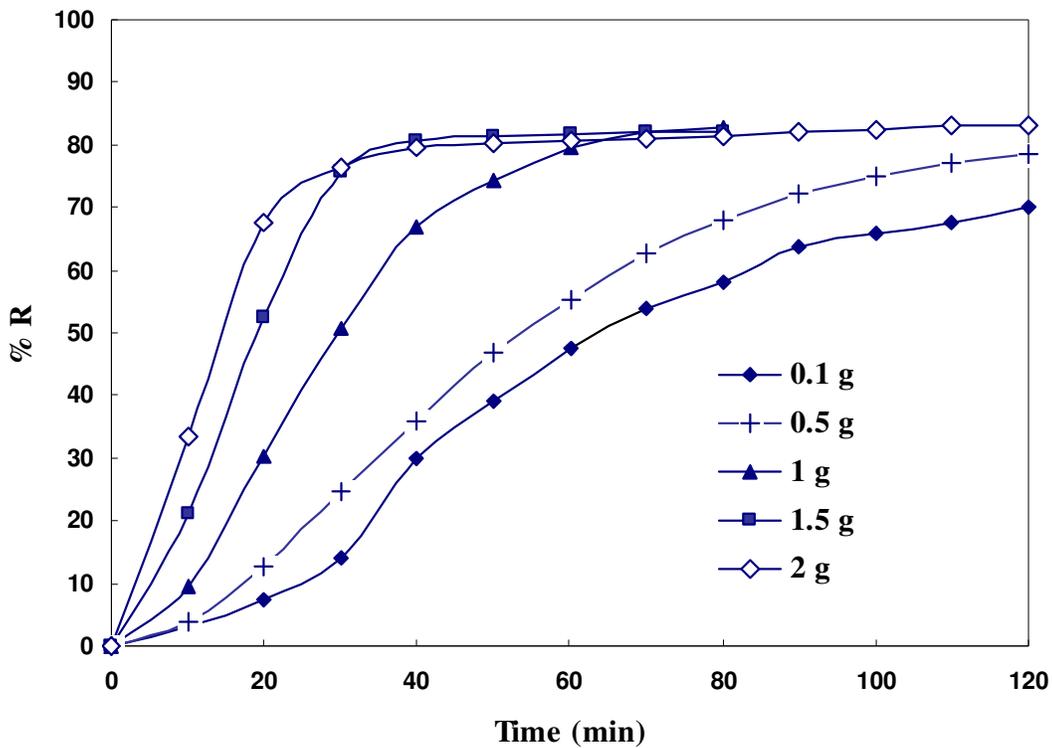


Figure 2. Effect of amount of HPPC on removal of BR 46 at:  $C_0= 15$  ppm,  $pH_i= 6.7$  and  $T= 25^\circ\text{C}$ .

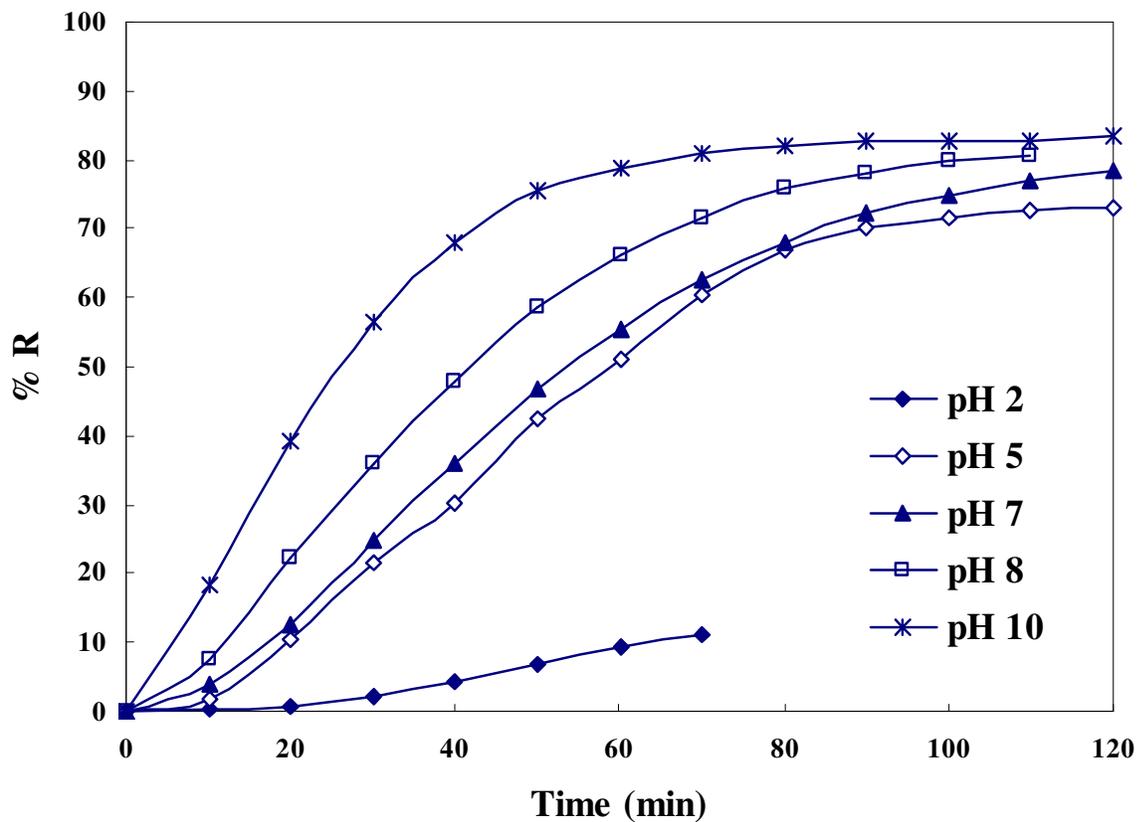
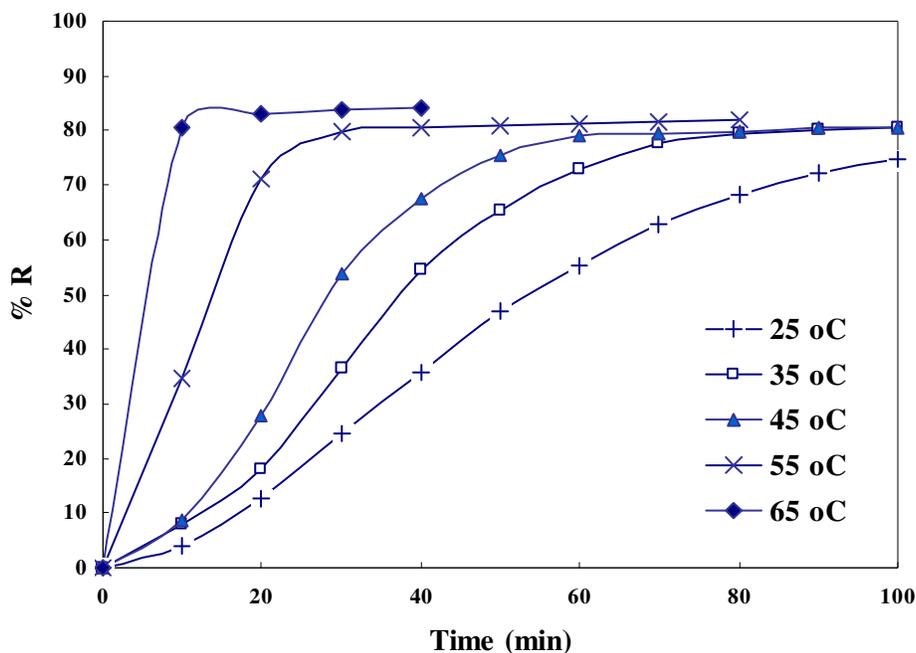


Figure 3. Effect of initial pH on removal of BR 46 at:  $C_0= 15$  ppm,  $m_i= 0.5$  g and  $T= 25^\circ\text{C}$ .



**Figure 4.** Effect of temperature on removal of BR 46 at:  $C_0= 15$  ppm,  $m_i= 0.5$  g and  $pH_i = 6.7$ .

positively charged thus making the  $H^+$  ions compete effectively with dye cations causing decrease in the amount of dye adsorbed ( $mg\ g^{-1}$ ). At higher pH, the surface of the HPPC gets negatively charged, which enhances the interaction of positively charged dye cations with the surface of HPPC through the electrostatic forces of attraction (Mall et al., 2007).

### Effect of temperature

Temperature is an important parameter for the adsorption process. A plot of BR 46 uptake as a function of temperature (25, 35, 45, 55 and 65°C), at the initial concentration of dye ( $C_0=15$  ppm), 0.5 g of HPPC and  $pH_i$  (6.7) is shown in Figure 4. From the figure, it is obvious that the removal percent of dye increases with increase in temperature from 25 to 65°C. A similar behavior has also been observed by Karagozoglu et al. (2007) for adsorption of Astrazon Blue FGRL onto sepiolite, fly ash and apricot shell activated carbon. The rise of adsorption with temperature could be due to the enlargement of the pore sizes of adsorbent particles at elevated temperatures (Namasivayam et al., 1995). Also, effective interaction between adsorbate molecules and adsorbent increases with increase in temperature.

### Effect of adsorbent size

The effect of adsorbent particles size on BR 46 uptakes for three different particles sizes (>1, 1-1.5, 2-3, 4-6 mm)

in the initial concentration 15 ppm of dye, 0.5 g of HPPC,  $pH_i$  (6.7) and temperature of 25°C is shown in Figure 5. It is obvious that for smaller particles, which have a higher solid - liquid interfacial area, the adsorption rate will be higher.

### BR 46 removal value after adsorption on HPPC via COD reduction measurement

The chemically dissolved oxygen (COD) of treated dye solutions was measured according to the standard methods for the examination of water and wastewater (Clesceri et al., 1989) at a fixed concentration of 15 ppm, 0.5 g HPPC, 25°C and  $pH_i$  (6.7) in various contact times. Initial COD value was 105 ppm. It is shown in Figure 6 that COD value decrease with increasing contact time.

### Study of adsorption modeling

Equilibrium adsorption isotherms play an important role in the predictive modelling that is used for the analysis and design of adsorption systems. These models are simple, give a good description of experimental behaviour in a large range of operating conditions and recharacterized by a limited number of adjustable parameters.

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Freundlich isotherm is expressed by Benefield et al. (1982) and Alley (2000).

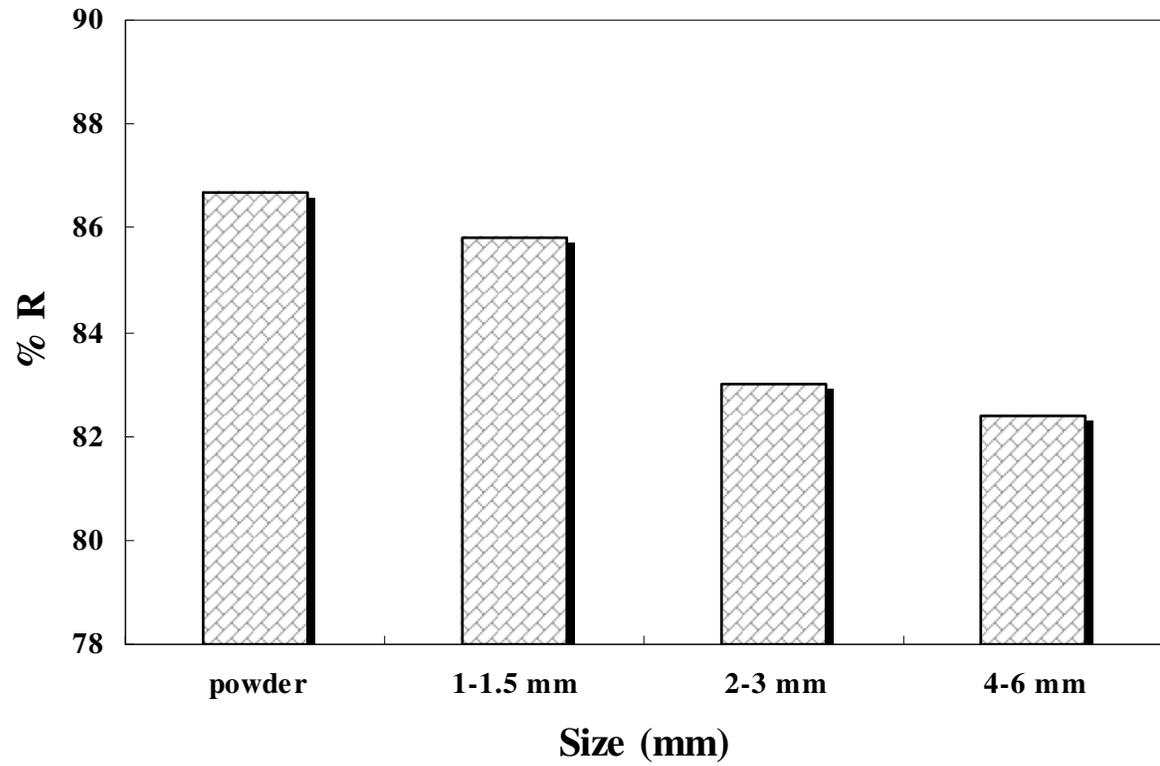


Figure 5. Effect of adsorbent particles size on removal of BR 46 at:  $C_0 = 15$  ppm,  $m_i = 0.5$  g,  $pH_i = 6.7$  and  $T = 25^\circ\text{C}$ .

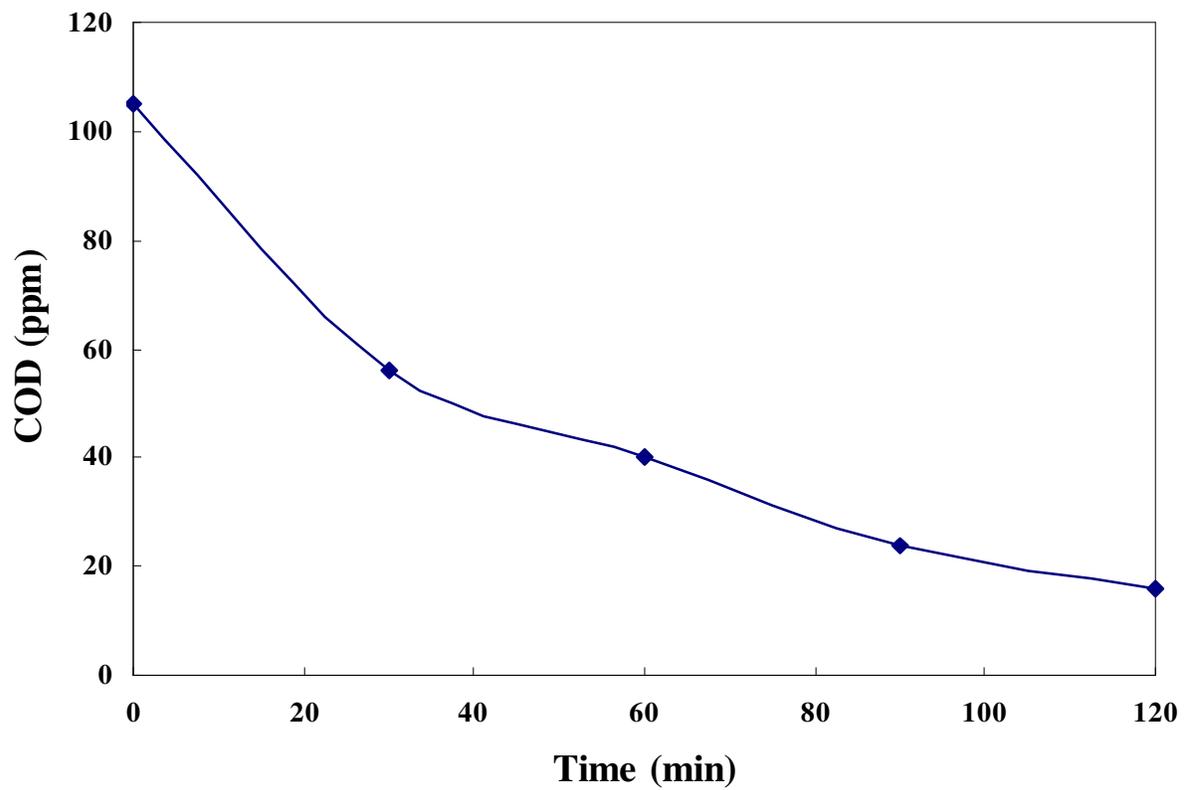
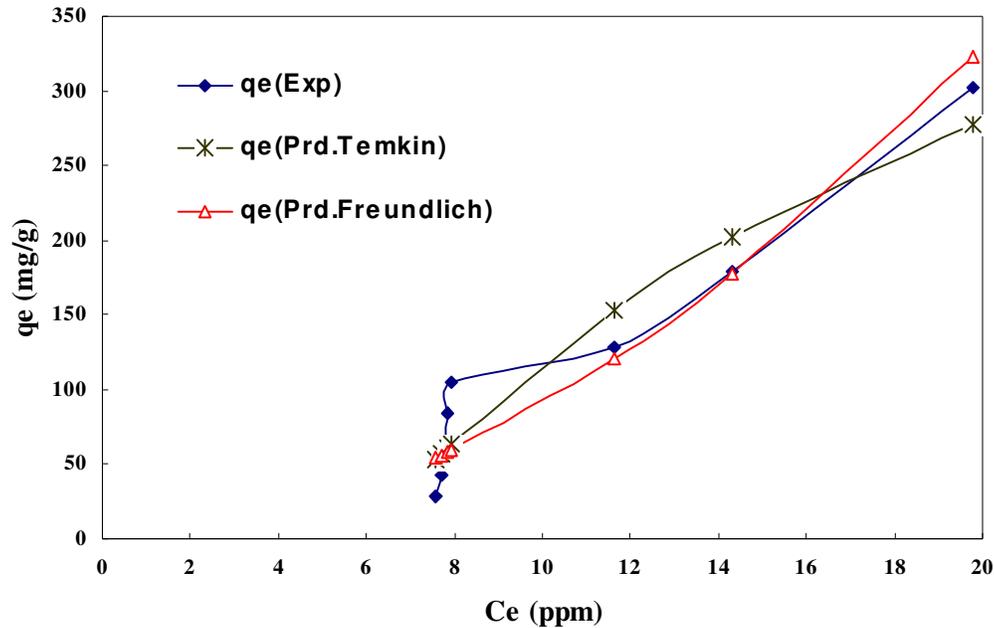


Figure 6. BR 46 removal.

**Table 2.** Isotherm constants for BR 46 onto HPPC by linear method.

Temkin	B	$K_T$	$r^2$
	1.799	0.165	0.908
Fruendlich	$1/n$	$K_f$	$r^2$
	1.858	1.265	0.753



**Figure 7.** The fit of experimental adsorption data to Freundlich and Temkin models for BR 46.

$$q_e = K_f C_e^{1/n} \tag{3}$$

Where  $q_e$  is the amount of dye adsorbed onto HPPC at equilibrium condition ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration of dye solution ( $\text{mg L}^{-1}$ ),  $K_f$  is adsorption capacity at unit concentration and  $1/n$  is adsorption intensity and they can be calculated from the plot of  $\ln q_e$  versus  $\ln C_e$ .  $1/n$  values indicate the type of isotherm to be irreversible ( $1/n = 0$ ), favorable ( $0 < 1/n < 1$ ), unfavorable ( $1/n > 1$ ) (Alley, 2000). Equation 3 can be rearranged to a linear form:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{4}$$

Temkin isotherm assumes that (1) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbate interactions and (2) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.

The Temkin isotherm is represented by Equation 5:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \tag{5}$$

Equation 5 can be expressed in its linear form as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{6}$$

Where,

$$B_1 = \frac{RT}{b} \tag{7}$$

The adsorption data can be analyzed according to Equation 6. A plot of  $q_e$  versus  $\ln C_e$  enables the determination of the isotherm constants  $K_T$  and  $B_1$ .  $K_T$  is the equilibrium binding constant ( $\text{L mg}^{-1}$ ) corresponding to the maximum binding energy and constant  $B_1$  is related to the heat of adsorption (Mall et al., 2007). The predicted isotherm constants for the BR 46 and their corresponding  $r^2$  values by the linear regression method are shown in Table 2. Also Figure 7 shows the fit of experimental

**Table 3.** Thermodynamic parameters for BR 46 onto HPPC.

$r^2$	$\Delta S$ ( $J K^{-1} mol^{-1}$ )	$\Delta H$ ( $kJ mol^{-1}$ )	$\Delta G$ ( $kJ mol^{-1}$ )				
			298 K	308 K	318 K	328 K	338 K
0.932	0.035	5.452	-5.007	-5.400	-5.608	-5.988	-6.469

adsorption data to Freundlich and Temkin models for BR 46 adsorption onto HPPC.

### Study of thermodynamic parameters

The thermodynamic parameters for the adsorption process,  $\Delta H$  ( $kJ mol^{-1}$ ),  $\Delta S$  ( $J K^{-1} mol^{-1}$ ) and  $\Delta G$  ( $kJ mol^{-1}$ ) were evaluated using the equations:

$$\Delta G = -RT \ln K_d \quad (8)$$

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

$$\ln K_d = \Delta S/R - \Delta H/RT \quad (10)$$

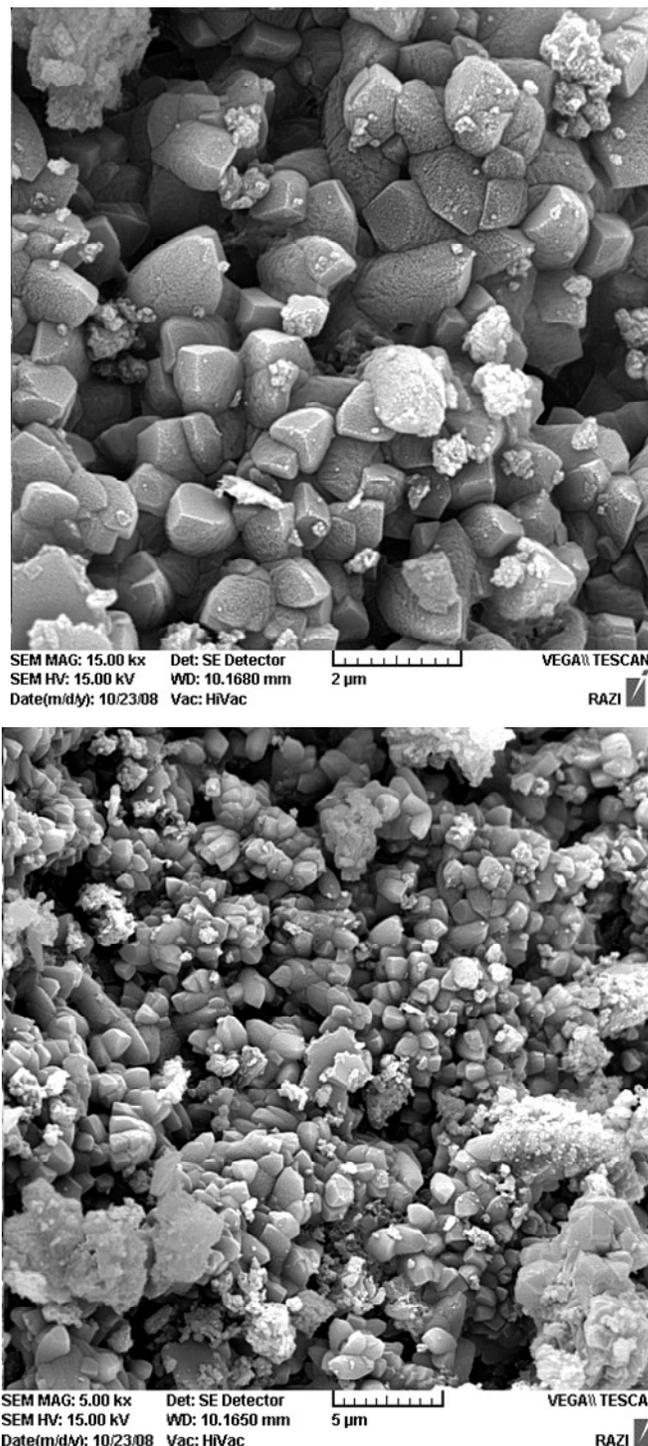
where  $K_d$  is the distribution coefficient of the adsorbate ( $K_d = q_e/C_e$ ),  $T$ , the absolute temperature (K),  $R$  (gas constant) =  $8.314 \times 10^{-3} kJ K^{-1} mol^{-1}$ . The plots of  $\ln K_d$  versus  $1/T$  could be utilized to find  $\Delta H$  and  $\Delta S$  which help to obtain  $\Delta G$  (Abou-Mesalam et al., 2003). Table 3 shows the data of thermodynamic parameters obtained from the adsorption of BR 46 at different temperatures. It is observed that the adsorption of BR 46 onto the HPPC was endothermic and spontaneous in nature with  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  values of  $+5.452 kJ \cdot mol^{-1}$ ,  $0.035 J \cdot K^{-1} \cdot mol^{-1}$  and  $-5.007 kJ \cdot mol^{-1}$  (288 K), respectively. The free energy changes  $\Delta G^\circ$  was evaluated with temperature increasing.

### SEM analysis

Scanning electron microscopy (SEM) has been an essential tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. It is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent. Scanning electron micrographs of HPPC is shown in Figure 8. From this figure it is clear that, HPPC has considerable numbers of pores where, there is a good possibility for dyes to be trapped and adsorbed into these pores.

### Conclusion

Hardened paste of Portland cement (HPPC), a low-cost building material, has considerable potential for the removal of BR 46 from aqueous solution. One of the major advantages of using HPPC for BR 46 removal over



**Figure 8.** SEM images of HPPC before treatment.

other chemical treatment methods is that it does not produce any chemical sludge. The present investigation shows that the removal was dependent on adsorbent dosage, contact time, pH and temperature.

The experimental data generated from batch adsorption experiments fitted well into the linearly transformed Temkin isotherm. This results suggests that HPPC was an efficient and economical adsorbent and may be helpful for waste water treatment.

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