INVESTIGATION OF DESORPTION KINETICS AND EQUILIBRIUM OF AN ANIONIC DYE FROM MAGNETIC POLYMER ADSORBENTS

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ABSTRACT

Dyes, which are used in different industries such as paper, plastics, leather, pharmaceutical, food, cosmetics, textiles, etc., constitute a major class of environmental pollutants. In recent studies, magnetic adsorbents combining magnetic separation technology with the adsorption process has been used to remove dyes from industrial wastewaters. The main advantages of the adsorbents are possible to be easily and simply separated from process media in a short time using the external magnetic field and will be reused. In present work, desorption behavior of the dye adsorbed particles was investigated. For this purpose, magnetic polymeric particles were used as adsorbents and Bromothymol Blue (BB) selected as an anionic dye. In order to determine the desorption pattern of the anionic dye from the magnetic polymeric particles, the particles were suspended in phosphate-buffered saline solution and maintained at 150 rpm. At predetermined time intervals, the samples were removed and the amount of desorbed BB was analyzed with a UV-vis spectrophotometer. The desorption kinetics and equilibrium of BB from the particles with time in pH 7.4 and 5 phosphate buffer solutions have clearly shown that the desorption of BB is affected by the characteristics (nano/micro) of the particles and there are significant differences in the desorption profiles between pH values.

Keywords: magnetic adsorbent, desorption, anionic dye, regeneration

1. Introduction

Adsorption processes have been widely used as an effective, efficient, and economic method for water purification. In recent studies, the adsorption features of polymer with the magnetic properties of iron oxides have been combined in polymeric particles to produce magnetic polymeric particles (Horak *et. al.*, 2007). These magnetic particles can be used as adsorbent for contaminants in water and after the adsorption is carried out, the adsorbent can be separated from the medium by a simple magnetic process.

In the adsorption process, desorption and regeneration of adsorbents are crucially important to keep low processing costs (Ip *et. al.*, 2009; Kyzas *et. al.,* 2014; Malekbala *et. al.*, 2015; Rego *et. al.*, 2013). Desorption studies are important not only because of process cost, but also to understand the nature of adsorbate-adsorbent interaction. For this purpose, desorption behaviors of the Bromothymol Blue (BB) adsorbed magnetic particles have been investigated in the present study. The desorption kinetics characteristics with time in pH 7.4 and 5 phosphate buffer solutions were also investigated.

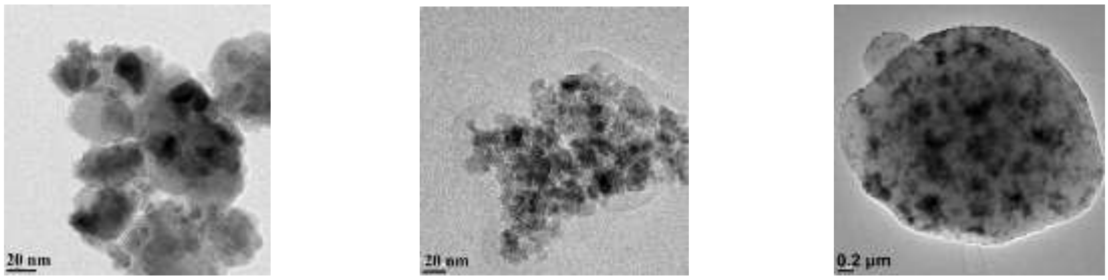
2. Materials and methods

Magnetic chitosan particles were synthesized using ionic gelation and suspension cross-linking methods. Detailed synthesis procedures of adsorbents were described in our previous reports (Akın *et al.*, 2013; 2015). In previously work, according to the characterization results, the particles were classified as the nanoparticles, which were synthesized by ionic gelation method (MPNs1); the nanoparticles (MPNs2) and microparticles (MPMs), which were synthesized by suspension cross-linking method. In order to determine the desorption properties of BB from the magnetic polymeric particles, the particles were suspended in phosphate-buffered saline solution and maintained at 150 rpm. At predetermined time intervals, the samples were removed and the amount of desorbed BB was analyzed with a UV-vis spectrophotometer. The surface compositions of bare magnetic polymeric particles and their BB adsorbed forms were characterized by energy dispersive X-ray diffraction spectroscope (EDX, LEO 1430 VP).

3. Results

3.1. Characterization of adsorbents

Previously classified particles as MPNs1, MPNs2 and MPMs are seen at the Figure 1. In the TEM images, darkness regions have shown the Fe_3O_4, lighter regions have shown presence of chitosan.



(a) **(b)** **(c)**

Figure 1: The TEM images of MPNs1**(a)**, MPNs2 **(b)** and MPMs **(c)**.

The EDX spectra reveal that C, O and Fe signals are existed in MPMs (Fig. 2 (a)), where Br signal appears along with other elements after treated with BB solution (Fig. 2 (b)). Also, same signals are existed in MPNs1 and MPNs2 (data not shown). A more detailed analysis of the chemical composition of the surface of BB adsorbed MPMs by elemental mapping taken with EDX is shown in Fig. 3, the presence of iron, oxygen, carbon and bromine is revealed for BB adsorbed MPMs.

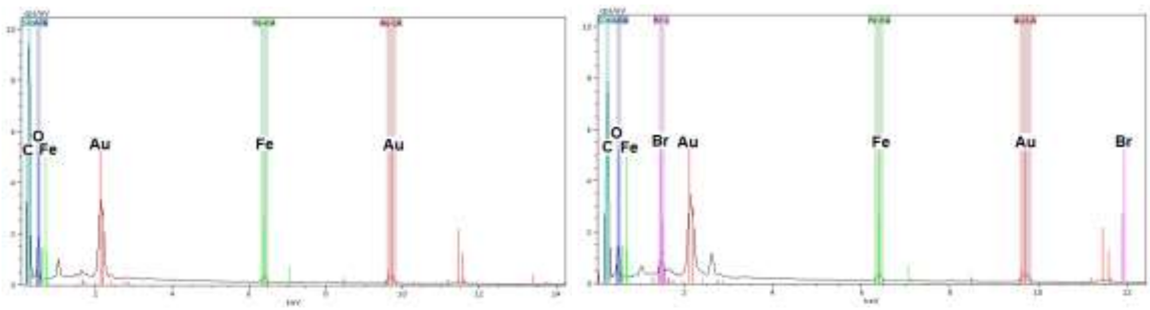


Figure 2: EDX spectra of MPMs **(a)** and BB-adsorbed MPMs **(b)**.

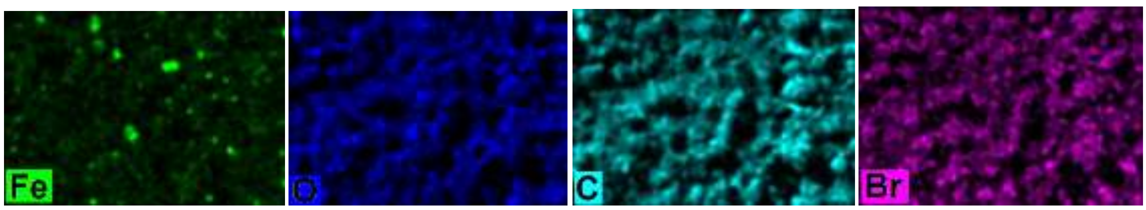
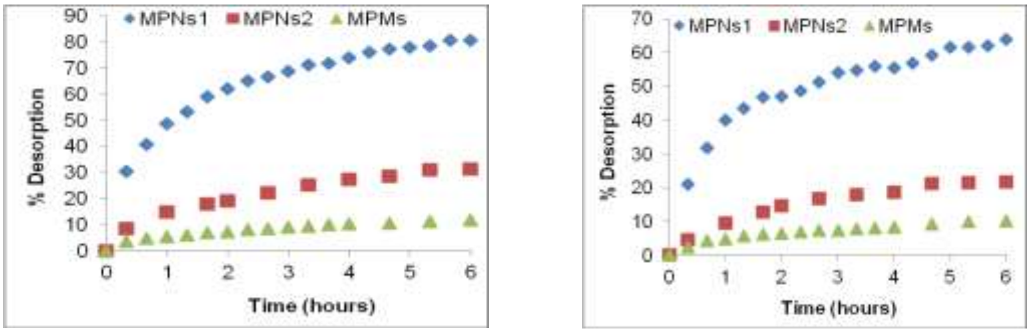


Figure 3: EDX elemental mapping of Fe, O, C and Br of BB adsorbed MPMs. The images that indicate the atomic symbols correspond to the EDX.

Desorption

The desorption behavior of the particles with time in pH 7.4 and 5.0 phosphate buffer solutions has been given at Figure 4.The desorption profiles of BB from the dye-loaded particles are clearly shown that the dye desorption is affected by the characteristics of the particles and there are significant differences in the desorption profiles between pH 7.4 and 5.0. It was observed that the desorption of the dye is favored at low pH values. The maximal desorption percentage of BB from MPNs1, MPNs2 and MPMs were 80.7 %, 31.2 % and 11.7 % within 6 hours, respectively. At pH 5.0, the maximal desorption amount of BB from MPNs1, MPNs2 and MPMs were obtained 85.29 mg/g, 21.83 mg/g and 20.98 mg/g, respectively. At lower pH, both the protonation of dye molecules and the positive charge of adsorbent surface increases. Thus, with the decrease in pH of medium, desorption increases. Also, the amount of dye removed from the surface of particles increased with decreasing particle size.



(a) **(b)**

Figure 4: Desorption of BB from magnetic chitosan micro and nanoparticles at pH 5.0 **(a)** and pH 7.4 **(b)**.

3.2. Kinetics models

Kinetics models, pseudo first order and pseudo second order were used to determine the adsorption behaviour.

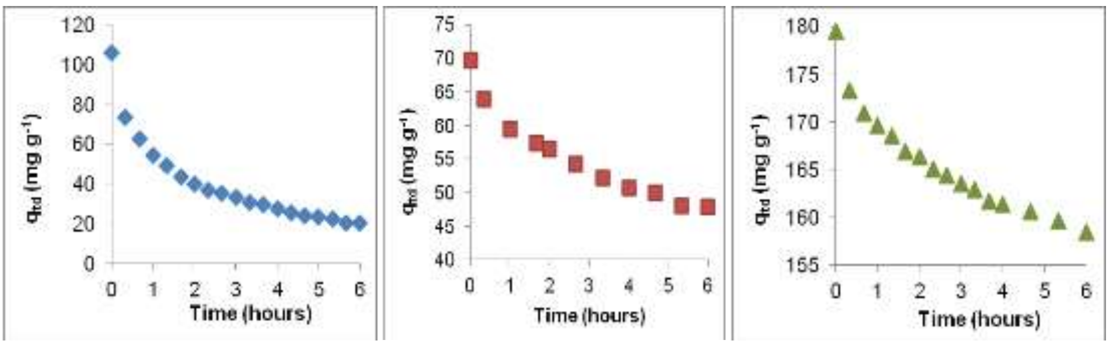
The pseudo first order model expressed as (Tseng *et. al.*, 2009):

$$\frac{dq_{td}}{dt} = -k_{1d}\left(q_{td}-q_{ed}\right) \quad (1)$$

The pseudo second order kinetics is given as (Tseng *et. al.*, 2009):

$$\frac{dq_{ed}}{dt} = -k_{2d}\left(q_{td}-q_{ed}\right)^2 \quad (2)$$

where k_{1d} and k_{2d} are the rate constants for pseudo first and second order kinetics models, respectively. qe and qt are the amount of dye adsorbed on the adsorbent (q) at equilibrium and any time t, respectively. The subscripts d denote the process of desorption.



(a) **(b)** **(c)**

Figure 5: Kinetics of desorption of BB from MPNs1**(a)**, MPNs2 **(b)** and MPMs **(c)**.

Figure 5 displays the kinetics of desorption BB from BB loaded adsorbents. It is observed from the figure that the desorption reaches equilibrium at 6 hours.

The linear plots of pseudo second order kinetics model are shown in Figure 6 and the parameters obtained from the models are presented in Table 1. All the experimental data showed beter compliance with pseudo second order kinetics model in terms of higher correlation coefficient values (R^2>0.95) and closer values between the calculated q_{ed} values ($q_{ed,cal}$) and the determined q_{ed} values by experiments ($q_{ed,exp}$).

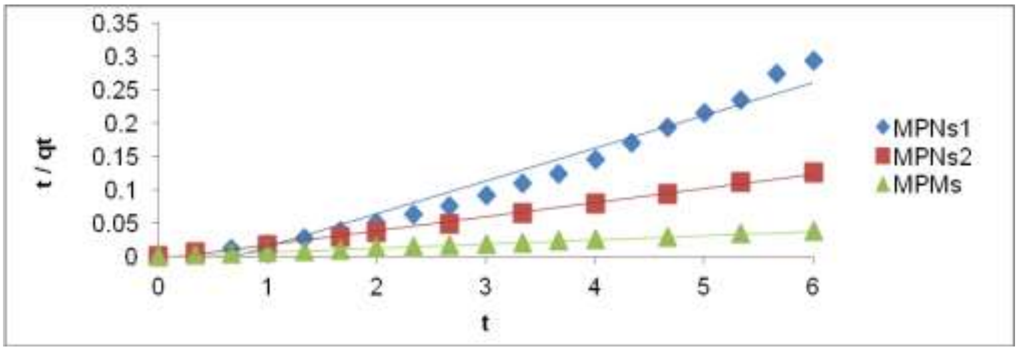


Figure 6: Pseudo second order kinetics for desorption of BB from MPNs1, MPNs2 and MPMs (pH 5.0, temperature: 25°C).

Table 1: Kinetics parameters for desorption of BB from the BB adsorbed adsorbent at initial pH value 5.0 and 25°C.

Adsorbent	$q_{ed,exp}$ (mg g^{-1})	First order kinetic model R^2	Second order kinetic model $q_{ed,cal}$ (mg g^{-1})	k_{2d} (g mg^{-1} hour^{-1})	R^2
MPNs1	20.40	0.8895	20.28	0.0691	0.9575
MPNs2	47.88	0.8261	47.39	0.1086	0.9964
MPMs	158.46	0.9878	158.73	0.0992	0.9997

4. Conclusions

In this research, desorption kinetics and equilibrium of an anionic dye from magnetic polymeric adsorbents were evaluated. The results indicate that the desorption of BB is affected by the characteristics (nano/micro) of the particles and pH of medium and the pseudo second order kinetics model is suitable to describe the desorption kinetics. The adsorbed BB could be desorbed efficiently and magnetic polymer nano and microparticles were recyclable. The adsorbents can be reused for the wastewater treatments.

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