Chemistry Letters Vol.32, No.6 (2003)

Fast Removal of Basic Dyes by a Novel Magnetic Nano-adsorbent

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(Received January 27, 2003; CL-030085)

A novel magnetic nano-adsorbent, prepared by covalently binding polyacrylic acid onto Fe_3O_4 magnetic nanoparticles, possessed high ion-exchange capacity and was successfully used for the fast removal of crystal violet.

Most adsorbents are sub-micron to micron-sized and have large internal porosities to increase their surface areas. However, the diffusion limitation within particles leads to the decrease in the adsorption rate and available capacity, particularly for macromolecules. Hence, it is important to develop an adsorbent with large surface area for adsorption and small diffusion resistance.[1] Magnetic nanoparticles have great applications in the fields of high-density data storage, ferrofluids, magnetic resonance imaging, bioseparation, and biomedicine.[2] They meet the above requirements and can be easily recovered or manipulated with an external magnetic field. Recently, we successfully bound the enzyme covalently on Fe_3O_4 magnetic nanoparticles via carbodiimide activation which has been widely used in conjugation reaction.[3,4] Following the similar approach, in this work, we develop a novel magnetic nano-adsorbent using Fe_3O_4 magnetic nanoparticles as cores and polyacrylic acid (PAA) as ionic exchange groups. Its use for the removal of basic dyes was studied, using crystal violet as a model compound.

Fe_3O_4 nanoparticles were prepared by coprecipitation method as described in our previous work.[3] For the binding of PAA, in general, 100 mg Fe_3O_4 nanoparticles and 0.5 mL carbodiimide (25 mg/mL in buffer A (3 mM phosphate, pH 6)) were added to 2 mL buffer A in sequence, and sonicated for 10 min. Then, 2.5 mL PAA (6–60 mg/mL in buffer A) was added and the reaction mixture was sonicated at 4 °C. The reaction was completed within 30 min. The product was recovered by a permanent magnet and then washed with buffer A.

The amount of PAA bound was determined from the percentage weight loss measured by the thermogravimetric analysis (TGA). In Figure 1, the TGA curve for Fe_3O_4 nanoparticles shows that the weight loss over 100–400 °C was only about 2%. However, for PAA-bound Fe_3O_4 nanoparticles, the TGA curve shows two weight loss steps. The first weight loss step over 100–250 °C might be due to the loss of residual water adsorbed physically in the sample. The sharp weight loss around 260 °C was due to the burning of PAA. From the inset in Figure 1, it was found that the amount of PAA bound on Fe_3O_4 nanoparticles (100 mg) increased first and then approached a constant (12 mg) with increasing the PAA amount (15–150 mg) in solution (5 mL). The maximum weight ratio of bound PAA to Fe_3O_4 was 0.12. So, the weight ratio of bound PAA to Fe_3O_4 was fixed at 0.12 in the following studies. Based on the density of Fe_3O_4 (5.18 g/mL) and the average molecular weight of PAA (180000), it was estimated that averagely two PAA molecules were bound to each Fe_3O_4 nanoparticle.

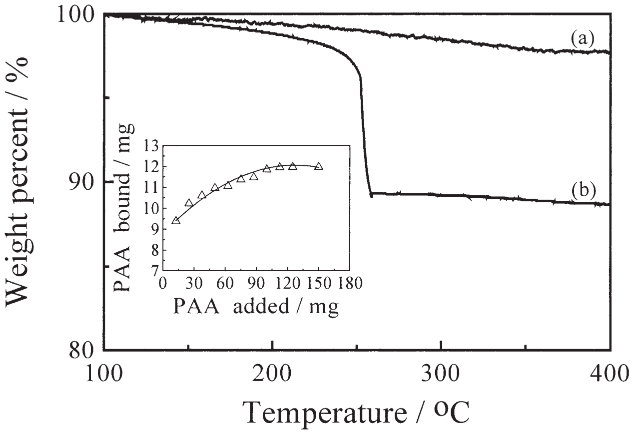

Figure 1. TGA curve of magnetic nanoparticles with without (a) and with (b) bound PAA. The inset illustrates the effect of the amount of PAA in solution on the amount of PAA bound on magnetic nanoparticles.

Figure 2 is the typical transmission electron microscopy (TEM) micrograph for PAA-bound Fe_3O_4 nanoparticles. They were essentially very fine with a mean diameter of 12 nm. In addition, the X-ray diffraction (XRD) analysis of PAA-bound Fe_3O_4 nanoparticles indicated six characteristic peaks at $2\theta =$ 30.1, 35.5, 43.1, 53.4, 57.0, and 62.6°, corresponding to their indices (220), (311), (400), (422), (511), and (440). This revealed that the binding process did not result in the phase change of Fe_3O_4. By Scherrer's equation,[5] the mean diameter of PAA-bound Fe_3O_4 nanoparticles also could be estimated as 11.6 nm, consistent with that observed from TEM micrograph.

For the determination of ion exchange capacity, 112 mg magnetic nano-adsorbent was first incubated in 5 mL 1.0 M NaCl. Since the preliminary experiment indicated the adsorption process reached equilibrium after mixing by vortex for

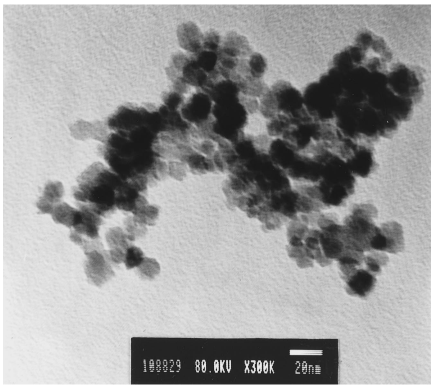

Figure 2. Transmission electron micrograph of magnetic nanoparticles with bound PAA. $PAA/Fe_3O_4 = 3/25$ w/w.

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about 1 min, magnetic nano-adsorbent was recovered magnetically after several minutes and then rinsed with water. Then, magnetic nano-adsorbent was added to 5 mL 1.0 mM HNO_3 to release Na^+ ions. After mixing for several minutes, the mixture was separated magnetically and the concentration of Na^+ ions in the supernatant was determined by inductively coupled plasma atomic emission spectrometry. It was found that the ionic exchange capacity was 1.64 mequiv./g, much higher than those of commercial ionic exchange resins (usually <0.1 mequiv./g[6]). In addition, the preliminary experiment revealed that the ionic exchange capacity of Fe_3O_4 nanoparticles for the adsorption of Na^+ ions was negligible (<0.02 mequiv./g). Hence, the ionic exchange capacity of magnetic nano-adsorbent was mainly attributed to the presence of PAA molecules. According to the amount of PAA bound and the degree of polymerization of PAA (2000–3000), the theoretical ionic exchange capacity of magnetic nano-adsorbent was estimated to be 1.38–1.67 mequiv./g, in agreement with the empirical value.

The adsorption of crystal violet on magnetic nano-adsorbent was investigated in deionized water at 25 °C. In general, 112 mg magnetic nano-adsorbent was added to 5 mL of crystal violet solution (0.1–6.3 mg/mL). After mixing for several minutes by vortex, magnetic nano-adsorbent was removed and the amount of crystal violet adsorbed was estimated from the concentration change of crystal violet in solution by the colorimetric method at 590 nm. Secondly, the removed magnetic nano-adsorbent was put into 5 mL methanol solution containing 1.0–8.0 vol% acetic acid.[2c] After mixing for several minutes, the concentration of crystal violet in solution was measured to estimate the amount of crystal violet desorbed. The adsorption and desorption measurements were conducted for the periods of 1 min to 24 h, and it was notable that both the equilibria were reached within 1 min.

Figure 3 shows the equilibrium isotherm for the adsorption of crystal violet on magnetic nano-adsorbent (22.4 mg/mL) in deionized water at 25 °C. The presence of a limit of adsorption amount revealed the adsorption behavior followed the Langmuir adsorption isothermal and could be described with the equation:[7] $C/q = 1/Kq_{\mathrm{m}} + C/q_{\mathrm{m}}$, where q is the adsorbed crystal violet concentration (mg/mg), C is the equilibrium crystal violet concentration in solution (mg/mL), q_{m} is the maximum amount of adsorbed crystal violet per mg of adsorbent (mg/mg) and K is the Langmuir adsorption equilibrium constant (mL/mg). As shown in the inset in Figure 3, the plot of C/q vs C yielded a straight line. From the slope and intercept, the values of q_{m} and K were estimated to be 0.116 mg/mg and 5.18 mL/mg, respectively. In addition, it was found that the adsorption amount of crystal violet (2 mg/mL) in 0.05 M phosphate buffer at 25 °C was not significantly affected by solution pH at 4–7, while slightly decreased with decreasing the solution pH at 2–4 due to the significant protonation of carbonyl groups. The adsorption at pH $>$ 7 was not examined because crystal violet could not be fully dissolved.

The study on the desorption of crystal violet revealed the percentage of crystal violet desorbed increased with increasing the content of acetic acid in methanol solution. When the content of acetic acid was increased up to 6 vol%, crystal violet could be completely desorbed. Furthermore, it was found that the magnetic nano-adsorbent retained chemical and physical stability when adsorption and desorption were repeated.

In conclusion, a novel magnetic nano-adsorbent has been successfully developed by the covalently binding of PAA on Fe_3O_4 nanoparticles. The adsorbent could be manipulated magnetically and exhibited quite high adsorption capacity and fast adsorption and desorption rates for the removal of basic dyes due to high specific surface area and the absence of internal diffusion resistance. The adsorbent should also be useful for the removal of other cationic solutes from aqueous solutions, particularly for those with large molecule weights.

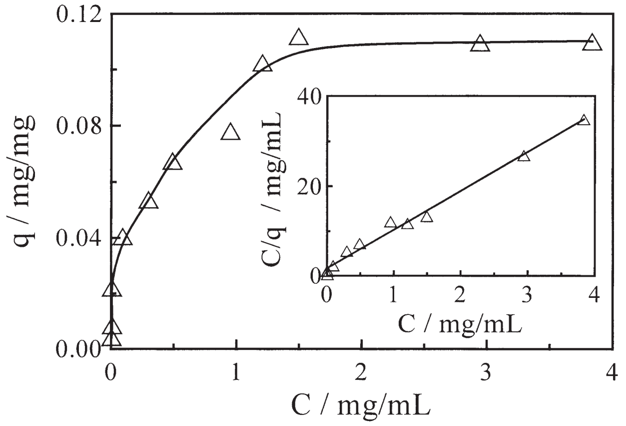

Figure 3. A plot of q vs C for the adsorption of crystal violet. The inset illustrates the linear dependence of C/q on C.

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Published on the web (Advance View) May 6, 2003; DOI 10.1246/cl.2003.488