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Removal of Reactive Red195 Synthetic Textile Dye using Polypyrrole-coated Magnetic Nanoparticles as an Efficient Adsorbent

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Abstract

Magnetic Fe_3O_4 nanoparticles modified by polypyrrole (PPy@Fe_3O_4 MNPs) was synthesized by chemical co-precipitation method and used as an adsorbent for removal of cationic dyes, Reactive Red195, from aqueous solutions. The resulting products are characterized by scanning electron microscope (SEM) and FT-IR. The effects of solution pH value, adsorbent amount, adsorption time and capacity of the nanocomposites have been fully investigated. The particles were showed to capture 99.0 mg g^{-1} of the dye within less than 10 min of contact time. Also, the sorption of Reactive Red195 dye was pH dependent and the higher efficiency of dye concentration removal was at pH 3.0. Experiments were carried out to investigate adsorption kinetics, adsorption isotherms and adsorption capacity. Kinetic data were well fitted by a pseudo second-order model. In the aqueous solution of Reactive Red195 dye at 25 °C, the adsorption data could be fitted by the Langmuir equation with a maximum adsorption amount of 99.0 mg g^{-1}. Moreover, the MNPs were recovered with over than 94% efficiency using methanol as elution agent.

Keywords: *Magnetic nano particle; Kinetic Model; Reactive Red 195; Textile dye.*

Introduction

The treatment and disposal of dye-contaminated wastewater is one of the most serious environmental problems faced by the textile, dyeing, printing, ink, and related industries. The common dyes include reactive,

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disperse, acid and basic, which usually have azo groups and aromatic structure that are harmful for human and ecosystem due to their toxicity and stability [1]. Even if they are non-toxic, residual dyes in wastewater absorb sunlight, leading to a decrease in the efficiency of photosynthesis in aquatic plants [2-4]. However, removal of color from wastewater is a great challenge. Therefore, it is necessary to find effective methods of wastewater treatment in order to remove color from effluents.

The methods used to the removal of organic dyes and pigments from wastewaters are classified into three main categories: (i) physical (adsorption, filtration, and flotation) [5, 6], (ii) chemical (oxidation, reduction, and electrochemical) [7, 8] and (iii) biological (aerobic and anaerobic degradation) [9, 10]. Among the different treatments described above, adsorption is attractive due the ease of operation and comparable low cost of application [11, 12]. Hence, because of the increasing attention on environmental protection, there is a growing demand for materials capable of removing various forms of organic contaminants or dyes from water surface. The common adsorbents primarily include activated carbons [13], highly porous materials [14], biomass and polymeric materials [15], etc. Although widely applied in research and practical applications, these materials still have limitations. For example, activated carbons and porous materials have the disadvantages such as difficulty in collection due to small particle size, high regeneration temperatures (e.g., 800-850 °C for activated carbon) and low separation efficiency caused by the co adsorption of water [16-18].

Therefore, efforts are still needed to carry out investigation for new promising adsorbents. More recently, magnetic porous materials were demonstrated to realize a fast separation of organic chemicals from water by applying an appropriate external magnetic field [19-22]. In fact, the application of magnetic particle technology to solve environmental problems has received considerable attention in recent years. Compared to the traditional adsorbents, they not only can be manipulated or recovered rapidly by an external magnetic field but also possess quite good performance owing to high efficient specific surface area and the absence of internal diffusion resistance [23, 24]. Application of conductive polymers is an alternative coating agent that can eliminate the mentioned drawbacks and improve selectivity [25]. Polyaniline [26], polypyrrole [27] and polythiophene [28] have extremely become popular for coating on the surface of nano material.

The magnetic separation provides suitable route for online separation, where particles with affinity to target species are mixed with the heterogeneous solution. Upon mixing with the solution, the particles tag the target species. External magnetic fields are then applied to separate the tagged particles from the solution.

In this work, polypyrrole-coated Fe_3O_4 MNPs were chemically synthesized and applied for removal of Reactive Red 195. Kinetic models and adsorption isotherm along with the effects of the pH of the sample solution, contact time and amount of MNPs on the adsorption efficiency of Reactive Red 195 were investigated. It is introduced as a simple, efficient and short time – consuming method to remove Reactive Red 195 from aqueous solutions.

Experimental

Chemicals

All chemicals were of analytical grade purity and used as received. Ferric chloride ($FeCl_3.H_2O$), ferrous chloride ($FeCl_2$. $4H_2O$), ammonia solution (25%), acetone, methanol and propanol were purchased from Merck (Darmstadt, Germany). Reactive Red 195 (RR195), an anionic textile dye, was purchased from Aldrich (Milwaukee, WI, USA). All other chemicals were from Merck (Darmstadt, Germany). A stock solution of 1000 mg L^{-1} RR195 was freshly prepared for each series of experiments. The standard working solutions were prepared daily by appropriate dilution of the stock standard solution with ultrapure water to the required concentrations. All the solutions were prepared with water purified by a Milli-Q system (Millipore, Bedford, MA, USA).

Apparatus

The UV-vis absorption spectra were obtained with a Model Cecil CE1010 (London, England), using a 1.0 cmquartz cuvette. A supermagnet with 1.4 Tesla magnetic field (10×5×4 cm) was used for magnetic separation. A Heidolph motor stirrer (Schwabach, Germany) was applied to stir dye solutions equipped with a glassware stirrer. All pH measurements were performed with a Model 713 pH Metrohm meter equipped with a combined glass electrode. A EM3200 scanning electron microscope (SEM, KYKY Zhongguancun, China) apparatus was used to investigate the size distribution and morphology of the PPy@Fe_3O_4 MNPs.

Preparation of polypyrrole-coated magnetic nanoparticles

A two-step strategy was used for synthesis of PPy@Fe_3O_4 MNPs previously reported in literature [29]. First, Fe_3O_4 nano particles were prepared by chemical co-precipitation method [30, 31] under a nitrogen atmosphere to avoid possible oxidization during reaction. The method is based on the following chemical reaction:

$$FeCl_2{\bullet}4H_2O + 2FeCl_3{\bullet}6H_2O + 8NH_4OH = Fe_3O_4(s) + 8NH_4Cl + 20H_2O$$

Briefly, 8.4 g of $FeCl_3.6H_2O$ and 2.25 g of $FeCl_2.4H_2O$ were dissolved in 400 mL deionized water via vigorous mechanical stirring under nitrogen atmosphere at 80 ºC. Then, 20 mL of ammonia solution (25%wt) was added dropwise into the above solution. The reaction was continued for 30 min at 80 ºC under constant stirring to ensure the complete growth of the nano particle crystals. After the reaction, the obtained MNPs precipitate was separated from the reaction medium by an external magnetic field, washed with deionized water several times and dried in a vacuum oven at 70 ºC for 5 h.

In the second step, 1.0 g of the dried Fe_3O_4 MNPs was added to 400 mL of deionized water at pH of 9.0 under stirring for 5 min and then, Then, the reaction mixture was further stirred for 10 min after adding 8.0 mL of pyrrole monomers. Subsequently, 1.5 g of $FeCl_3$•$6H_2O$ was dissolved in 50 mL of deionized water and added drop wise to the mixture under stirring. After the addition of oxidant, the mixture was stirred for 12 h at room temperature. The obtained PPy@Fe_3O_4 MNPs were recovered from the reaction mixture using a permanent magnet and washed several times with ethanol and then dried at 50 ºC under vacuum for 3 h.

Removal procedure

Adsorption of dye on PPy@Fe_3O_4 MNPs was studied by batch experiments. A stock solution (1000 mg L^{-1}) of dye was prepared from analytical-reagent product. The stock solution was then diluted to give a series of standard solutions in different concentrations. Typically, adsorption volume of solution was 25 mL and 25 mg PPy@Fe_3O_4 MNPs were used in each adsorption. At given time intervals, the suspension containing adsorbents was extracted and adsorbents were collected using an adscititious magnet. Dye concentration in supernate after magnetic separation was monitored by UV–Vis spectrophotometer at λmax = 464.9 nm. The removal efficiency of dye was calculated using the following equations, respectively:

Dye removal efficiency (%) = $(C_0\text{-}C_r/C_0) \times 100$

where C_0 and C_r are initial dye concentration (mg L^{-1}) and instantaneous dye concentration (mg L^{-1}), respectively.

Results and discussion

Characterization of PPy@Fe_3O_4 MNPs

SEM was used to determinate the size and morphology of synthesized PPy@Fe_3O_4 MNPs. According to Fig. 1, the PPy@Fe_3O_4 MNPs have a nearly spherical shape with a smooth and uniform surface morphology with average particle size less than 80 nm.

The FT-IR analysis was also used for more confirmation of PPy coating. Both bare and PPy@Fe_3O_4 MNPs were analyzed by FT-IR between 4000 and 400 cm^{-1} and the obtained spectra are shown in Fig. 2 A and B, respectively. Two characteristic absorption peaks at 3400 cm^{-1} and 580 cm^{-1} in Fig. 2 (A and B) are attributed to the stretching vibrations of hydrogen-bonded surface water molecules as well as hydroxyl groups and the Fe-O transverse vibration, respectively. The appearance of characteristic PPy bands in spectrum (B) confirms the coating of PPy on the surface of Fe_3O_4 NPs. The weak bands at 2800 and 2900 cm^{-1} are corresponding to the stretching vibrations of C-H bonds. The absorption peak at 1050 cm^{-1} is assigned to the bending vibration of C-H bond in the pyrrole ring. The absorption band at 1314 cm^{-1} indicates the C-N stretching vibration. The absorption bands at 1549 and 1460 cm^{-1} could be attributed to C-C asymmetric and symmetric stretching vibrations of the pyrrole ring, respectively. Finally, successful coating of PPy on the surface of Fe_3O_4 NPs can be concluded from the obtained results.

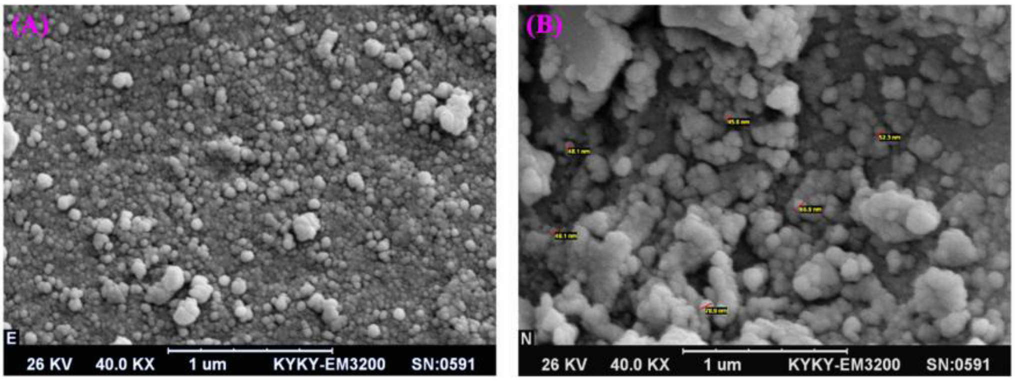

Figure 1. SEM micrographs of PPy@Fe_3O_4 MNPs at (A) 20,000× and (B) 40,000× magnifications.

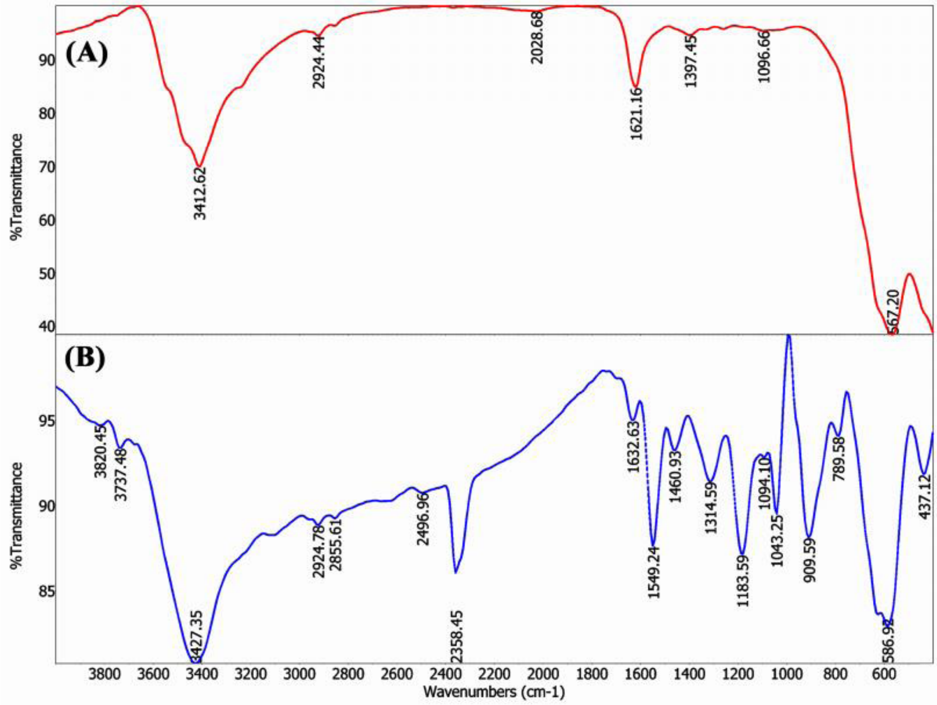

Figure 2. FT-IR spectra of (A) bare Fe_3O_4 NPs and (B) PPy@Fe_3O_4 MNPs.

Effect of pH

Solution pH is an important parameter that affects adsorption of dye molecules due to its influence on the surface properties of the adsorbent and ionization/dissociation of the dye [32]. Firstly, an investigation was taken on

UV spectra of the dye solution in the various pH ranges of 3 to 12. The results reveal that, there are no changes in color absorbance and wavelengths within pH variation. This phenomenon is strongly confirmed that every change can be attributed to interaction of dye with PPy@Fe_3O_4 MNPs.

In order to study the effect of pH on RR195 adsorption on Fe_3O_4 MNPs, experiments were conducted at varying pH range of 3 to 12 with 50 mg L−1 initial dye concentration with 25 mg magnetic particle at the room temperature (±27^{o}C) for the 10 min equilibrium time. In the acidic medium, (pH = 3.0) the nanoparticles have positive surface charge. Thus, under this circumstance, the nano particles can interact with anion dye molecules, and then it was chosen as the optimum pH (Fig. 3). In the lower pH, the positive charge density on the surface of PPy@Fe_3O_4 MNPs can be formed, under these conditions; the uptake of negative charged dye will be high and resulting in enhanced removal of dye. In addition, PPy@Fe_3O_4 MNPs can absorb part of the dyes because of the hydrophobic interaction between the dyes and the adsorbent.

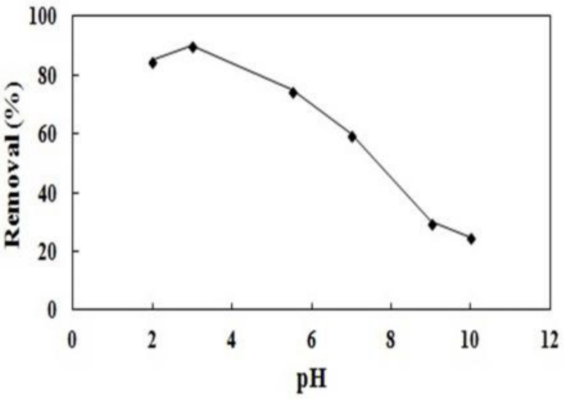

Figure 3. Effect of pH on the adsorption of dye on MNPs. (RR195: 25 mL, 50 mg L^{-1}, agitation time =10 min, 25 mg PPy@Fe_3O_4 MNPs).

Effect of adsorbent amount

Adsorption dosage is another important parameter because it determines the capacity of an adsorbent for a given initial concentration of adsorbate. To determine the effect of adsorbent dosage on RR195 adsorption, experiments were conducted by varying the adsorbent dosage in the sample solution for a fixed initial dye concentration of 50 mg L−1, room temperature (±27^{o}C), 200 rpm shaking speed and pH 3.0 with contact time of 10 min. After a dye removal, the MNPs were separated with an external magnetic field from sample solution and the residue concentration of supernatant was determined. As the adsorbent dosage increases, the surface area of the adsorbent will be increased and, more adsorption sites are available to absorb RR195 from aqueous solution. Hence, it was found that an increase in amount of absorbent up to 25 mg increased the removal efficiency. At higher amounts, no considerable changes in removal efficiency were observed (Figure 4)

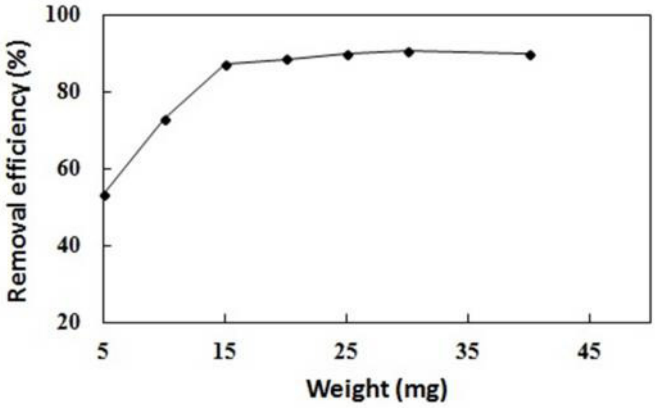

Figure 4. Effect of different amount of MNPs on removal efficiency. (pH = 3.0, RR195: 25 mL, 50 mg L^{-1}, agitation time =10 min).

Effect of contact time

The contact time between adsorbate and adsorbent is one of the most important design parameters that affect the performance of adsorption processes. The effect of contact time on removal efficiency was studied at the range of 0 to 60 min. The experiments were carried out in 25 mL of dye solution with pH of 3.0 (50 mg L^{-1}, 25 mg PPy@Fe_3O_4 MNPs, and room temperature). The contact time required to achieve equilibrium and complete adsorption for dye. Therefore, According to figure 5, the optimum contact time between sample solution and PPy@Fe_3O_4 MNPs was considered to be 10 min.

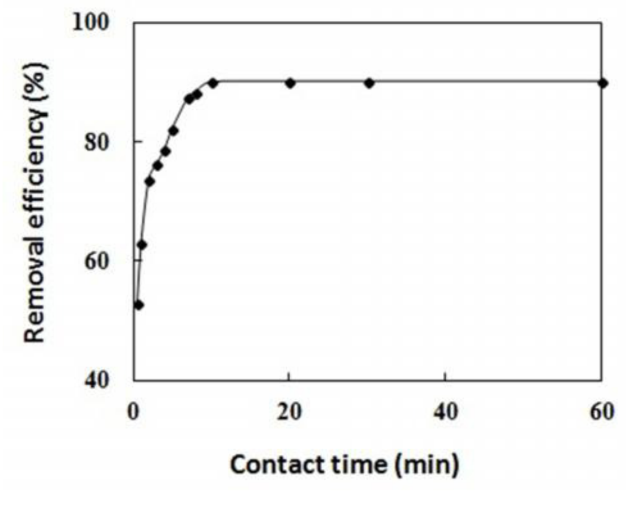

Figure 5. Effect of contact time on adsorption efficiency. (pH = 3.0, RR195: 25 mL, 50 mg L^{-1}, 25 mg PPy@Fe_3O_4 MNPs).

Adsorption kinetics

To find out the rate-controlling step of the adsorption process, establishing well defined kinetic models is needed [33]. Several adsorption kinetic models have been established to understand the adsorption kinetics and the rate-limiting step. The pseudo-first-order, pseudo-second-order and intraparticle diffusion models are the well-known models to study the adsorption kinetics and quantify the extent of uptake in adsorption kinetics [34]. These models were calculated using the following equations, respectively:

Pseudo-first-order model: $$\ln (q_e - q_t) = \ln q_e - K_1 t \quad (1)$$

Pseudo-second-order model: $$t/q_t = 1/K_2 q_e^2 + 1/q_e \quad (2)$$

Intraparticle diffusion model: $$q_t = K_3 t^{1/2} \quad (3)$$

Where qe and qt (mg g^{-1}) are the amounts of dyes absorbed in equilibrium and at time t (min); and k1 (min^{-1}), k2 (g mg^{-1} min^{-1}) and k3 (mg g^{-1} min^{-1}/2) are the kinetic rate constants for the pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The correlation coefficients (R2) were used to confirm the agreement between experimental data and the model-predicted values.

Kinetic studies were performed in a glass beaker, where 25 mg of PPy@Fe_3O_4 MNPs were added into 25 mL of the dye solution with 50 mg L^{-1} at ambient temperature. The agitation speed of the motor stirrer was fixed at 200 rpm during the experiments. The residual dye concentration in the solution was analyzed using spectrophotometer during the intervals ranging from 0 to 60 min. According to the fig. 6 and correlation coefficient, the experimental data fit to the pseudo-second-order model ($R^2 > 0.99$) better than other models, which indicates that the rate-limiting step might be the chemical adsorption, whereas fitting of kinetic data to a pseudo-first-order and intraparticle diffusion models resulted in R^2 values of 0.969 and 0.957, respectively (figure 6).

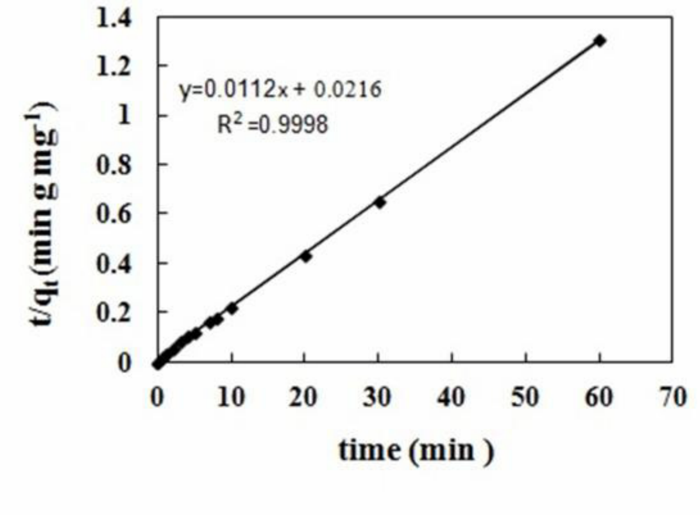

Figure 6. Fitting of kinetic data to pseudo-second order kinetic model.

Adsorption isotherm

The adsorption isotherm describes the relationship between adsorbent and adsorbate, usually the ratio of the quantity absorbed and remained in the solution at equilibrium at a fixed temperature [35, 36]. The Langmuir and Freundlich models are used to describe the process of adsorption. In this work, the isotherm data were analyzed using two most common isotherm models: Langmuir and Freundlich. The Langmuir model assumes that adsorption occurs at specific localized sites on a homogeneous surface by the monolayer formation of an adsorbates onto the adsorbent surface [37, 38] and The Freundlich isotherm model is an empirical equation valid for the adsorption of a reversible heterogeneous surface[39].

Both the linearized forms of Langmuir and Freundlich equations are given by the following equations, respectively:

$$C_e/q_e = 1/K_L q_m + 1/q_m \quad C_e \qquad (3)$$

$$L \quad q_e = L \quad K_F + (1/n)L \quad C_e \qquad (4)$$

where C_e is the equilibrium dye concentration into the sample solution (mg L^{-1}), qe is the amount of dye absorbed per gram of adsorbent (mg g^{-1}) at Ce, qmax is the maximum sorption capacity (mg g^{-1}) which depends on the number of adsorption site. K_L and K_F are the Langmuir and Freundlich constants (L mg^{-1}) respectively and n (dimensionless) is the heterogeneity factor.

The adsorption capacities of the as-obtained PPy@Fe_3O_4 MNPs to dye were measured individually at pH 3.0 with 25 mg of PPy@Fe_3O_4 MNPs and varied dye concentration.

The obtained correlation coefficients (R_2 Langmuir = 0.991, R^2 Freundlich = 0.836) showed that the adsorption equilibrium could be better fitted with the Langmuir isotherm rather than Freundlich isotherm (n = 0.74), which indicated the homogeneous distribution of active sites on the surface of PPy@Fe_3O_4 MNPs. The maximum monolayer capacity qmax and K_L that calculated by Langmuir model were as 99.0 mg g^{-1} and 0.081 L mg^{-1}, respectively (Figure 7).

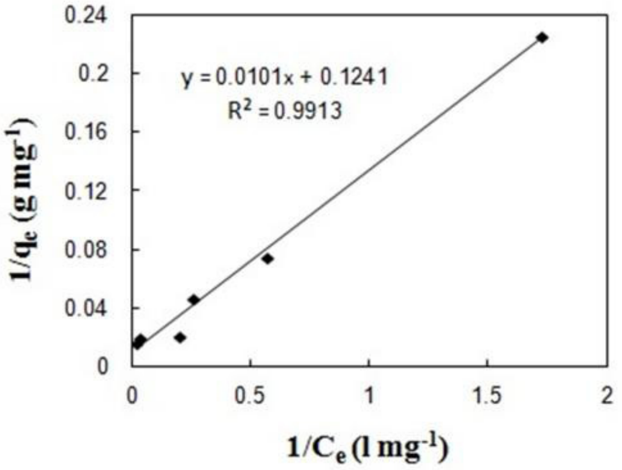

Figure 7. Langmuir adsorption isotherm of dye for MNPs.

Desorption and reused study

The key to the success of adsorptive removal of dyes by MNPs primarily depends on the desorption/regeneration ability of dye loaded MNPs for their reuse. In principle, an ideal desorption/regeneration process should restore the initial characteristics of adsorbent for its possible reuse.

In fact, to promote desorption efficiency, desorption experiments were performed with three eluents including methanol, acetone and propanol because organic dyes dissolved easily in organic solvents. To evaluate the reused ability of adsorbent, several adsorption/desorption cycles were carried out. The desorption ability of methanol was found higher than the other solvents. The results showed that desorption efficiency higher than 94% can be achieved in a short time of 2 min and in a one step elution using 2 mL of methanol after 7 cycles of adsorption/desorption.

Conclusion

A novel magnetic nano-adsorbent was fabricated by modifying the surface of Fe_3O_4 nanoparticles with Polypyrrole which was characterized by SEM and FT-IR analysis. The time required to achieve the adsorption equilibrium was 10min. The experimental data of adsorption kinetics fit to the pseudo-second-order model better than pseudo-first-order mode and the adsorption behavior is consistent with the Langmuir better than Freundlich isotherm. According to the Langmuir isotherm model, the maximum adsorption capacity for

RR195 was 99.0 mg g^{-1}. Furthermore, from economical point of view the adsorbent can be reused with convenient condition. The sorption of pollutants from aqueous solutions plays a significant role in water pollution control. High removal efficiency, fast adsorption and simplicity of the magnetic separation from sample body are the advantages that make the PPy@Fe_3O_4 MNPs as unique adsorbents for removal of RR195.

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