Extraction of 2-Hydroxyphenol by Surfactant Coated Nanosized Magnetic Particles

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Abstract−A colloidal suspension of magnetic particles coated with double layer surfactant molecules was prepared, characterized and used for separation of some chemicals. The aqueous magnetic fluid was prepared by chemical precipitation method and characterized by total organic carbon analyzer (TOC), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). The TOC and TGA measurements indicate that the prepared magnetic particles are coated with surfactant molecules in double layers. The outer surfactant layer has free polar heads. TEM measurement results show that magnetic particles are nanosized. A mixture of 2-hydroxyphenol (strong polar) and 2-nitrophenol (weak polar) was chosen as the target system. Results show that the magnetic fluid can selectively adsorb 2-hydroxyphenol from the mixture, whereas the adsorption of 2-nitrophenol is insignificant. For 2-hydroxyphenol, the adsorption equilibrium can be described well by Langmuir isotherm, and the adsorption kinetic can be fitted well by a linear driving force mass transfer model.

Key words: Nano-sized Magnetic Particles, Bi-layer Surfactant Coating, 2-Hydroxyphenol, 2-Nitrophenol, Adsorption Equilibrium, Adsorption Kinetics

INTRODUCTION

Magnetic separation technology deals with the transportation of magnetic or magnetically susceptible particles in an external magnetic field.

Magnetic separation technologies, according to the characteristics of target systems, can be divided into two types: 1) the separation of magnetic target by the external magnetic field; and 2) the separation of non-magnetic target by forming a complex with magnetic particles, which can interact with, and therefore be separated by the external magnetic field. Wastewater treatment using magnetic microorganisms [Bahaj et al., 1998] and metal recovery [Waton and Li, 1999] are under the first category. The second type mainly deals with enzyme immobilization [Dekker, 1989; Kondo and Fukuda, 1997], cell sorting [Haik et al., 1999; Hancock and Kemshead, 1993; Honda et al., 1999; Molday and Molday, 1984], protein adsorption and purification [Dietrich et al., 1998; O'Brien et al., 1997], nucleic acid detachment [Levison et al., 1998; Uhlen, 1989] and drug delivery [Rusetski and Ruuge, 1990]. Most of the published work is classified as the second type separation.

Under the second type, magnetic particles in suspensions can be divided into three groups according to their sizes: magnetic fluids (0.01-0.1 μm), unstable suspensions of larger ferroparticles (1-10 μm), and magnetic microspheres (complex construction of 0.1-10 μm particles) [Ruuge and Rusetski, 1993]. To achieve the separation goal, magnetic particles are coated with some intermediates, such as surfactants or specific ligands to achieve the separation. The target molecules are bonded to the magnetic particles through the intermediates. External magnetic field is used to maneuver the separation process.

Large size magnetic particles are usually used as solid matrix for the batch process of adsorption or immobilization of targets. The disadvantage of the separation using large size magnetic particles is that the permanent magnetization of large size magnetic particles can cause the agglomeration even after the remove of external magnetic field.

Magnetic fluids, which are also named ferrofluids, are stable colloidal suspensions of nanometer-sized magnetic single-domain particles that are coated with one or two layers of surfactants and dispersed in a liquid medium [Rosensweig, 1985]. Fendler [2001] reviewed applications of various types of surfactant-coated particles including magnetic particles. Several works have been published on the preparation of double layer coated magnetic fluids. Preparation of magnetic fluid with double layer surfactant coating by chemical precipitation method was first published in 1978 [Shimoiizaka, 1978]. Since then, a few more works have been published on preparation of double layer coated aqueous magnetic fluids [Akhavan and Ghominezhad, 1998; Wooding et al., 1991]. A thorough study on synthesis and characterization of double layer coated magnetic fluid was reported in 1999 [Shen et al., 1999].

The potential use of magnetic fluid as a separation method mainly depends on its structure, unique characteristics, fluid-like behavior, intermediate's properties and magnetic properties. Superparamagnetic properties make magnetic fluid sensitive to respond to the external magnetic field.

Most of the published work on magnetic fluid deals with the preparation and characterization of surfactant coated colloidal suspension of magnetic particles. Only a limited number of studies have been published on adsorption of biomolecules on surfactant-coated magnetic particles. One previous work studied the adsorption equilibrium and kinetics of bilayer phospholipids (unilamellar vesicles) onto Fe_3O_4 nanocolloids coated with single layer lauric acid [De Cuyper and Joniau, 1991]. However, the role of lauric acid on the

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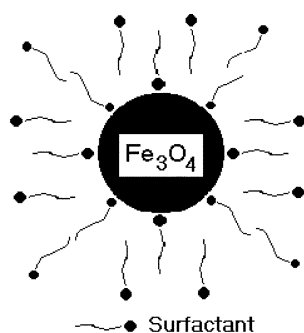E-mail: cheshahb@nus.edu.sg

Fig. 1. Core-shell structure of bilayer coated magnetic particle.

adsorption mechanism of the phospholipids was not established from the study.

The main objective of the present work was to use a bilayer surfactant-coated magnetic particles for the separation of chemicals. The prepared magnetic particles have a bilayer surfactant coated structure as shown in Fig. 1, which has free polar heads at the outer layer. A system of 2-hydroxyphenol and 2-nitrophenol is chosen for the adsorption study based on their polarity. The study includes the equilibrium and the kinetics of the adsorption process and some characterizations of the magnetic particles.

MATERIALS AND METHODS

1. Materials

Iron (II) chloride tetrahydrate (99%) was obtained from Fisher (USA). Iron(III) chloride hexahydrate (98%) was obtained from Nacalai Tesque (Japan). Ammonium hydroxide (25%), acetone, methanol, phosphoric acid (85%) were purchased from Merck (USA). Undecanoic acid, 2-hydroxyphenol, 2-nitrophenol were purchased from Aldrich (USA). All the chemicals were used as received without further treatment. The water used in this work was Milli-Q ultra pure water.

2. Preparation of Aqueous Magnetic Fluids

The chemical precipitation method [Shen et al., 1999; Wooding et al., 1991] was used to prepare aqueous magnetic fluids coated with double layer undecanoic acid. The method is based on the following chemical reaction [Elmore, 1938]:

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

A complete precipitation of Fe_3O_4 is achieved under alkaline condition, while maintaining a molar ratio of $Fe^{2+} : Fe^{3+} = 1 : 2$ under a non-oxidizing environment. To obtain 1 g of Fe_3O_4 precipitate, 0.86 g of $FeCl_2 \cdot 4H_2O$ and 2.36 g $FeCl_3 \cdot 6H_2O$ were dissolved under N_2 atmosphere in 40 ml of de-aerated Milli-Q water with vigorous stirring (1,000 rpm). As the solution was being heated to 80 °C, 1 g of the undecanoic acid and 5 ml NH_4OH were added together. To ensure the complete growth of the nanoparticle crystals, the reaction was carried out for 30 min at 80 °C under constant stirring. The resulting water-based suspension was cooled down to room temperature and then washed with acetone and methanol to remove the unreacted surfactant. The residual methanol and acetone from the precipitated magnetic particles were then removed by washing with Milli-Q water. This methanol/acetone wash will not affect the ad-

sorbed surfactant [Shen et al., 1999]. The washed magnetic particles were resuspended into 25 ml Milli-Q water, and the slurry was heated to 60 °C with constant stirring. Once the slurry reached 60 °C, a surfactant solution of pH 10 (prepared by dissolving 1 g undecanoic acid to 10 ml of Milli-Q water in presence of NH_4OH) was added dropwise until a stable suspension was obtained. At this point, a dull black colored suspension turned to a shiny dark reddish brown color. A stable suspension does not produce any visible precipitation when placed on a magnet for about 5 min.

3. Characterization of Magnetic Fluids

The characterizations of the magnetic nanoparticle are carried out to study its properties. TOC and TGA are used to study the double layer coated structure, whereas TEM is used to measure the size of magnetic particle.

To prepare dried samples for the analysis, the second coated magnetic particles in suspensions were precipitated completely in an ultracentrifuge (Beckman Ultracentrifuge, 20 min at 40,000 rpm). Both the second coated magnetic particles obtained from the centrifuge and the first coated magnetic particles obtained through washing were dried (Edwards freeze-dryer, ESM 1342) for 48 h to remove as much water as possible. TOC test was performed by QT Astro 2100 model TOC analyzer. The total carbon content was obtained from the TOC result. TGA test was performed by a TA 2050/winNT thermal analysis system. 10 mg of the dried sample was loaded into the system, and the mass loss of the sample was monitored under N_2 atmosphere at temperatures from 25 to 600 °C at a rate of 20 °C per minute.

A bright-field TEM (JEM-2010) was used for the size measurement of the magnetic nanoparticles. To prepare the sample for TEM measurement, a copper film (200 mesh and covered with formvar/carbon) was coated with a thin layer of diluted magnetic fluid. The copper film was then dried at room temperature for 24 h before the measurement.

4. Separation Experiment

2-hydroxyphenol and 2-nitrophenol were used as a model system to test the adsorption characteristics of magnetic fluid coated with double layer undecanoic acid. Both the equilibrium and the kinetics of the adsorption process were investigated.

4-1. Equilibrium Study

For equilibrium studies, 0.3 ml magnetic fluid with a solid fraction of 0.0139 (g/ml) was mixed with 3 ml feed solution of different concentrations. The feed was either of 2-hydroxyphenol or 2-nitrophenol, or equimolar mixture of these two components. All the experiments were conducted at pH of 6.6, which was the unadjusted pH of the mixture of magnetic fluid and feed solution. After three days, the magnetic particles settled naturally, giving a clear supernatant suitable for HPLC analysis without any further treatment. The effect of pH on the adsorption of 2-hydroxyphenol was also studied.

4-2. Kinetics Study

The adsorption kinetics of 2-hydroxyphenol on magnetic fluid was studied at two different initial feed mixture concentrations, 0.0826 mM and 0.1719 mM. Several identical samples were prepared by mixing 0.3 ml magnetic fluid and 3 ml feed solution and stored in separate bottles. At different time intervals, the supernatant from each of the sample bottles were withdrawn for analysis.

5. Analytical Methods

The concentrations of 2-hydroxyphenol and 2-nitrophenol were measured by Jasco HPLC system equipped with a reverse phase column (HP ZORBAX C-18) under the following conditions: column temperature 35 °C, UV wavelength 275 nm, mobile phase: acetonitrile (45%) and phosphoric acid (0.01 M) (55%), flow rate 1.0 ml/min.

HPLC analysis requires the sample to be completely free from magnetic particles. During equilibrium study, the samples were collected after 72 hours and by this time, all the magnetic particles had settled naturally, giving a clear supernatant free of magnetic particles. Similar sample collection procedure was not applicable for kinetic study, when samples were collected at time intervals. The magnetic particles needed to be separated from the solution quickly after the sample was collected in order to avoid any further adsorption of 2-hydroxyphenol on the particles. Methanol was added to the collected sample to accelerate the precipitation of the magnetic particles. The settled particles were held by a magnet and the clear supernatant was withdrawn for solute analysis by HPLC. It has been found experimentally that the solute concentrations in the supernatants, obtained through long time natural precipitation and by accelerated precipitation through methanol addition, do not show any significant difference.

RESULTS AND DISCUSSION

A magnetic fluid was synthesized, characterized and used for the separation studies. The results are discussed in the following sections.

1. Structure of Magnetic Particles

The TOC results of single and double coated magnetic particles are shown in Fig. 2. The TOC curve of monolayer magnetic particles has shown one peak compared to two peaks for the bilayer magnetic particles. From the TOC results, the amount of surfactant on monolayer coated and bilayer coated particles are calculated as 0.0763 g and 0.1457 g per gram of particles, respectively. The TGA measurement results are given in Fig. 3. It shows that about 16% mass loss is found for single coated particles, whereas for bilayer
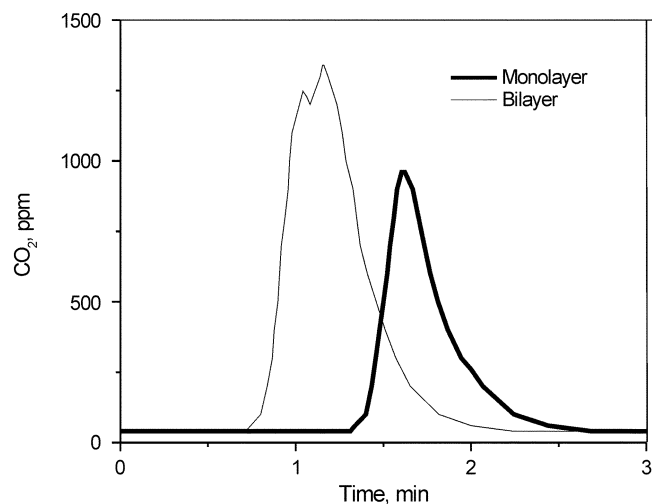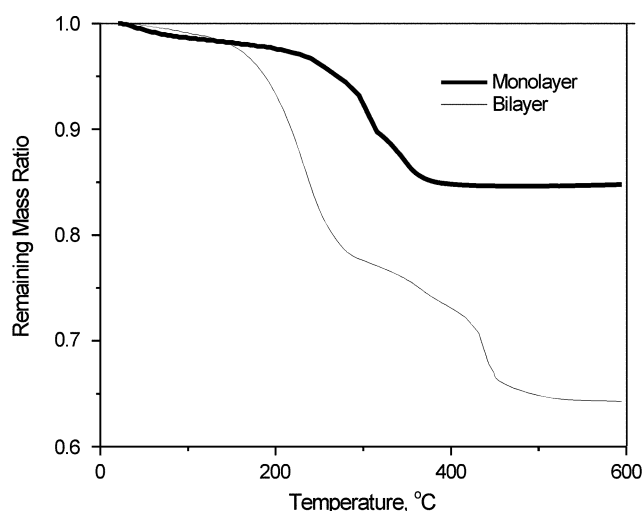

Fig. 3. TGA curve for monolayer and bilayer surfactant coated magnetic particles.

Fig. 4. TEM micrograph of bilayer coated magnetic particles.

Fig. 2. TOC curve for monolayer and bilayer surfactant coated magnetic particles.
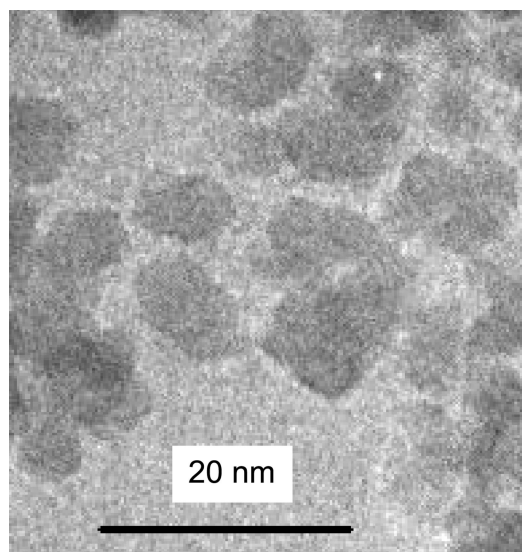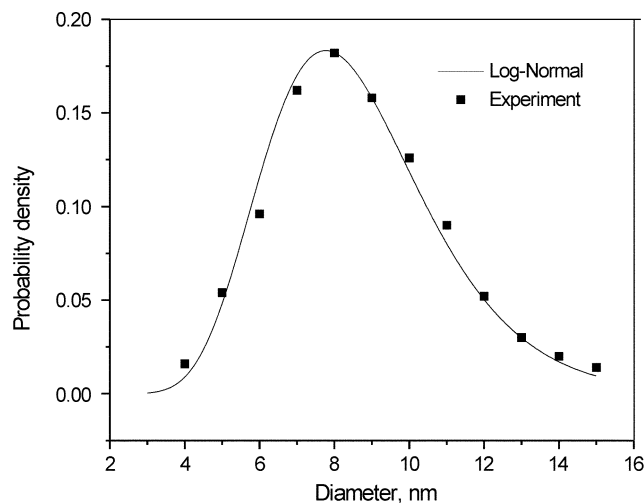

Fig. 5. Size distribution of magnetic particles.

coated particles the mass loss is about 37%. Both TOC and TGA results are consistent and indicate core-shell type bilayer surfactant coating structure of the magnetic particles. Similar results were obtained by previous work [Shen et al., 1999].

2. Size of Magnetic Particles

Magnetic particles' size and the distributions are determined from TEM micrographs. A typical TEM picture is shown in Fig. 4.

The sizes of 500 particles from the TEM results were measured and the size distribution found to be log-normal as shown in Fig. 5. The mean diameter of the particles is calculated from the following log-normal equation:

$$p(D) = \frac{1}{D\alpha\sqrt{2*\pi}} \exp\left[-\frac{1}{2*\sigma^2}\left(\ln\frac{D}{D_0}\right)^2\right] \tag{1}$$

Where, $p(D)$ is the probability frequency, D is the diameter, D_0 is the mean diameter and σ is the standard deviation.

The mean particle diameter as calculated from the distribution is 8.36 nm (σ=1.31). This shows that the prepared magnetic particles have superparamagnetic properties (particle size less than 30 nm) [Berkovsky et al., 1993] and it can form stable dispersion (particle size less than 15.5 nm) [Rosensweig, 1985].

3. HPLC Analysis Results

Typical HPLC chromatogram for 25 ppm mixture of 2-hydroxyphenol and 2-nitrophenol is shown in Fig. 6. This shows that 2-hydroxyphenol is more polar than 2-nitrophenol. It is commonly known that in an HPLC system where a stationary phase is less polar than the mobile phase, it is expected that the more polar compound in the mobile phase will be eluted first [Knox, 1982].

4. Effect of pH on the Adsorption Equilibrium of 2-hydroxyphenol

Effects of pH on the adsorption of 2-hydroxyphenol by magnetic fluids are shown in Fig. 7. Results show that the adsorption is strongly influenced by the solution pH. Highest adsorption has occurred at pH between 6 and 7. This may be explained in terms of the isoelectric point of the particles. Isoelectric point of magnetic particles is 6.5 [Iwasaki et al., 1962], which falls in the pH range
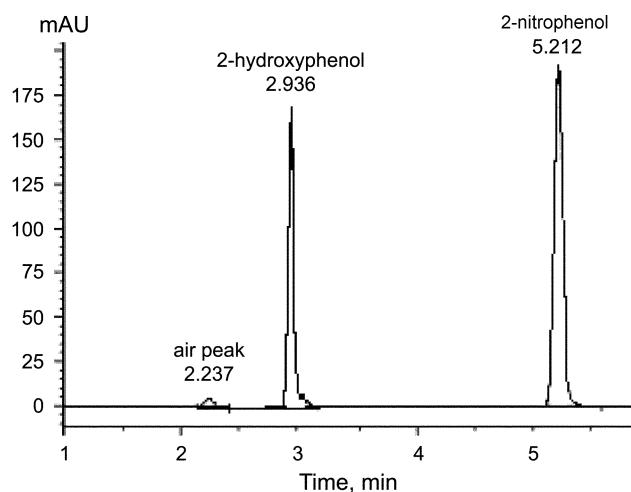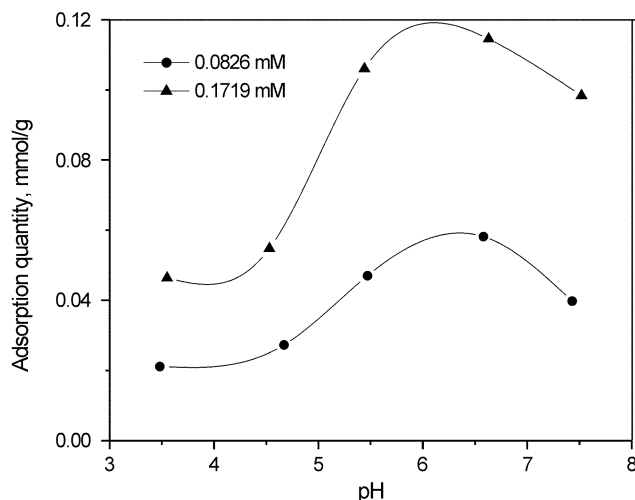

Fig. 7. Effect of pH on equilibrium adsorption of 2-hydroxyphenol on magnetic particles (initial concentration of 2-hydroxyphenol in the mixture of feed and magnetic fluid: 0.0826 mM and 0.1719 mM).
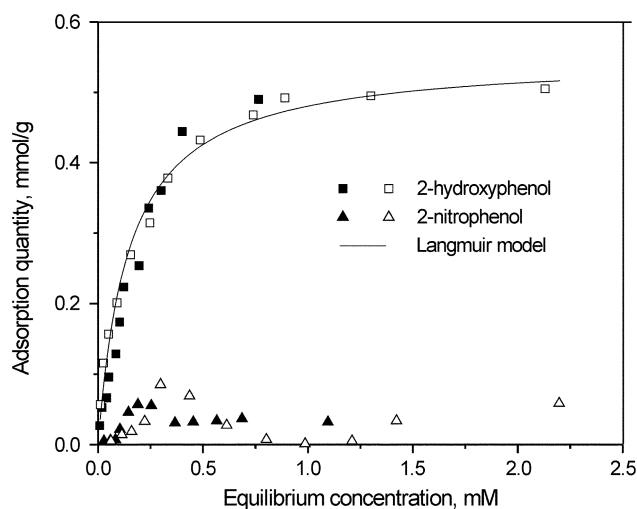

Fig. 8. Equilibrium isotherm of 2-hydroxyphenol and 2-nitrophenol (blank label is for single component adsorption, solid label is for mixture adsorption).

for maximum adsorption. All the subsequent adsorption equilibrium and kinetic studies were conducted at a pH of about 6.6, which is the unadjusted pH of the mixture of magnetic fluid and feed solution.

5. Adsorption Equilibrium of 2-Hydroxyphenol and 2-Nitrophenol

Fig. 8 shows the adsorption equilibrium for 2-hydroxyphenol and 2-nitrophenol, which are obtained either from a single component or binary mixture feeds experiments.

Results show that the prepared magnetic particles can selectively adsorb 2-hydroxyphenol in a much higher capacity than 2-nitrophenol. This confirms that the prepared magnetic particles have a free polar head outer layer, which can selectively adsorb the polar compounds.

Results also show that the presence of 2-nitrophenol in the feed

Fig. 6. Typical HPLC diagram for 25 ppm 2-hydroxyphenol and 2-nitrophenol (column temperature 35 °C, UV wavelength 275 nm, mobile phase: acetonitrile (45%) and phosphoric acid (0.01 M) (55%), flow rate 1.0 ml/min).

does not have any significant influence on the selectivity of adsorption between the two compounds.

The experimental equilibrium adsorption data for 2-hydroxyphenol are fitted to the following Langmuir isotherm through non-linear regression analysis:

$$Q = \frac{Q_m K_a C^*}{1 + K_a C^*} \quad (2)$$

Where, Q is adsorbed quantity (mmol/g solid), Q_m is maximum adsorbed quantity (mmol/g solid), K_a is equilibrium coefficient (mM^{-1}), C* is equilibrium solution concentration (mM).

Fig. 8 shows that the Langmuir isotherm can describe well the adsorption experimental data with a correlation coefficient of R^2= 0.986. Q_m=0.551 mmol/g solid and K_a=6.797 mM^{-1} are obtained from the fitting.

6. Adsorption Kinetics

Adsorption kinetics of 2-hydroxyphenol on magnetic particles were studied at two different feed concentrations, and the results are shown in Fig. 9. The two different feed concentrations studied do not have significant effect on the kinetics of the process.

A linear driving force mass transfer model is used to describe the adsorption kinetics. The model can be expressed as:
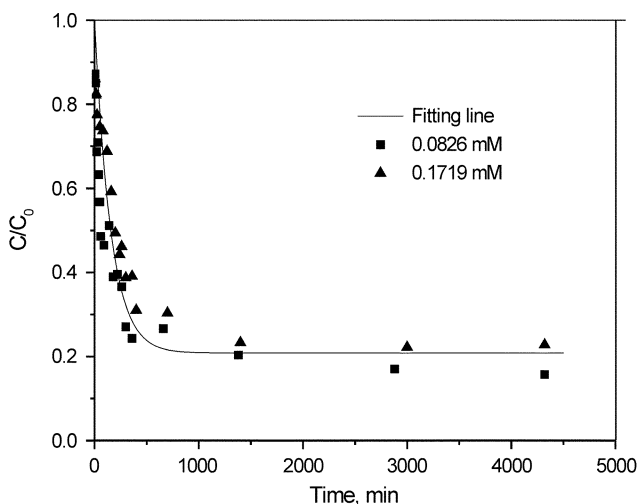
$$-\frac{dC}{dt} = K_L a(C - C^*) \quad (3)$$

Where, $K_L a$ is the overall mass transfer coefficient, C is the concentration of 2-hydroxyphenol in solution at time, t, and C* is equilibrium concentration.

C* is obtained from Langmuir isotherm [Eq. (2)] and the resulting equation becomes:

$$-\frac{dC}{dt} = K_L a\left(C - \frac{Q}{Q_m K_a - Q K_a}\right) \quad (4)$$

The mass balance of 2-hydroxyphenol can be expressed as:

$$C_0 V = CV + SQ \quad (5)$$

Where, C_0 is the initial concentration of 2-hydroxyphenol, V is the volume of the feed mixture and S is the solid content of magnetic fluid.

Substituting Eq. (5) into Eq. (4), the following differential equation is obtained:

$$-\frac{dC}{dt} = K_L a\left(C - \frac{\frac{(C_0 - C)V}{S}}{Q_m K_a - K_a \frac{(C_0 - C)V}{S}}\right) \quad (6)$$

Eq. (6) is integrated numerically by using a standard routine such as Polymath 4 for solving non-linear ordinary differential equations. The fitted curve and the experimental data are compared in Fig. 9. It is found that the experimental results are fitted well with $K_L a$= 0.005 (min^{-1}).

CONCLUSIONS

The following conclusions can be drawn from the present study: The magnetic fluid prepared by chemical precipitation method contains nanosized magnetic particles with double layer surfactant coating and can form a stable dispersion. The magnetic particles can selectively adsorb 2-hydroxyphenol from mixture of 2-hydroxyphenol and 2-nitrophenol on the basis of polarity. Adsorption equilibrium of 2-hydroxyphenol follows Langmuir isotherm. Adsorption kinetics of 2-hydroxyphenol fits well in a linear driving force mass transfer model.

ACKNOWLEDGEMENTS

NOMENCLATURE

C   : concentration of 2-hydroxyphenol [mM]
C_0 : initial concentration [mM]
C*   : equilibrium concentration [mM]
D   : diameter of magnetic particles [nm]
D_0 : mean diameter of magnetic particles [nm]
K_a : equilibrium coefficient [mM^{-1}]
$K_L a$: overall mass transfer coefficient
p(D) : probability frequency [dimensionless]
Q   : adsorbed quantity [mmol/g solid]
Q_m : maximum adsorbed quantity [mmol/g solid]
S   : solid content of magnetic fluid [g]
t   : time [min]
V   : volume of the feed mixture [ml]
σ : standard deviation of log-normal distribution

Fig. 9. Adsorption kinetics of 2-hydroxyphenol on magnetic particles (initial concentration of 2-hydroxyphenol in the mixture of feed and magnetic fluid: 0.0826 mM and 0.1719 mM).

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