Effect of functional groups on sludge for biosorption of reactive dyes

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Abstract

The sludge, which was collected from a biological coke wastewater treatment plant, was used as a low-cost adsorbent in the removal of reactive dyes (Methylene Blue (MB) and Reactive Red 4 (RR4)) from aqueous solution. The pH of dye solution played an important role on the dye uptake. With the solution pH increase, the MB uptake increased; whereas the RR4 uptake decreased. The maximum uptake of RR4 by protonated sludge was 73.7 mg/g at pH 1, and the maximum uptake of MB by sludge was 235.3 mg/g at pH 9. Three functional groups, including carboxyl, phosphonate, and amine group, were identified by potentiometric titration, fourier transform infrared (FT-IR) spectrometry, and X-ray photoelectron spectroscopy (XPS). The anionic functional groups, phosphonate and carboxyl group, were identified as the binding sites for the cationic MB. Amine groups were identified to bind RR4. The main mechanism of the reactive dyestuffs adsorption is electrostatic interaction.

Key words: sludge; reactive dyes; mechanism

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Introduction

Dyes are commonly used in many industries, such as food, paper, rubber, plastics, and textile (Robinson *et al.*, 2002). The presence of dyes in the effluent discharged from these industries is highly visible and undesirable even at very low concentration (Nigam *et al.*, 2000). Moreover, dyes may affect photosynthetic activity in aquatic systems by reducing light penetration (Aksu and Tezer, 2000; McMullan *et al.*, 2001), and several commonly used dyes have been reported to be carcinogenic and mutagenic for aquatic organisms (Chen *et al.*, 2003). Dye-containing wastewater is very difficult to be degraded, since dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents (Sun and Yang, 2003). Most technologies presently employed for dye removal are based on physicochemical processes, such as dilution, adsorption, coagulation and flocculation, chemical precipitation, oxidation, ion-exchange, reverse osmosis and ultra-filtration (Crini, 2006; Robinson *et al.*, 2001). Among these processes, physical adsorption technology is attractive for the dye treatment from the wastewater, due to its easy availability, simplicity of design, high efficiency, ease of operation, and ability to treat dyes in more concentrated form (Meshko *et al.*, 2001). Activated carbons are widely used as adsorbents because of their high adsorption abilities for a large number of organic compounds. However, the price of activated carbons is relatively high, which limits their usage (Faria *et al.*, 2004; Nakagawa *et al.*, 2004).

Biosorption processes, which can be defined as the uptake of contaminants via various physico-chemical mechanisms by inactive/dead biological materials, are relatively easy to operate and posses several inherent advantages, including low cost, operation over a wide range of conditions and possible reuse of biosorbents (Volesky and Schiewer, 1999). Many biosorbent, including bagasse pith, maize cobs, sunflower, peat, orange peel, saw dust, corynebacterium glutamicum (Crini, 2006; Won *et al.*, 2005), bentonite, steel-plant slag, fly ash (Ramakrishna and Viraraghavan, 1997), China clay (Gupta *et al.*, 1992), waste slurry (Yun, 2004), and rice husk (Kumar and Bandyopadhyay, 2006), have been used to remove contaminants from wastewater. In biosorption processes, numerous groups presented that for certain biosorbents (Yun, 2004; Yun *et al.*, 2001), carboxyl, carbonyl, sulfonate, sulfhydryl, phosphonate, and hydroxyl groups have proposed to contribute to binding contaminants.

In this study, adsorption performance of the sludge in removal reactive dyes (Methylene Blue (MB) and Reactive Red 4 (RR4)) from aqueous solution was evaluated under various conditions and the mechanism was also investigated.

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1 Materials and methods

1.1 Materials and chemicals

The finely ground sludge was treated with 1 mol/L HNO_3 solution for 24 h to replace the natural mix of ionic species with protons. The acid-treated sludge was washed several times with deionized distilled water to remove the excess acid. It was then dried in an oven at 60°C for 24 h. The resulting dried protonated sludge was stored in a desiccator and used as the adsorbent in sorption experiments.

All chemicals used in this study were of analytical grade. The model reactive dyes Methylene Blue and Reactive Red 4 were purchased from AppliChem, China and Sigma-Aldrich Korea Ltd., respectively. The general characteristics of MB and RR4 are shown in Table 1.

Table 1 General characteristics of Methylene Blue (MB) and Reactive Red 4 (RR4)

Dye	Chemical formula	Molar mass	Color index number	Dye content (%)	λ_{max} (nm)
MB	$C_{14}H_{18}ClN_3S$	319.86	52015	85	663
RR4	$C_{32}H_{23}ClN_8Na_4O_{14}S_4$	995.23	17757	50	517

1.2 Dye adsorption procedure

In the adsorption experiments, a constant mass of protonated sludge (0.15 g) was weighed into a 50-mL high-density polyethylene bottle and 30 mL of dye solution were added. The mixture was shaken at 160 r/min at (25 ± 2)°C. The pH of the solution was adjusted using 0.1 mol/L HCl or 0.1 mol/L NaOH. After 24 h, the sludge was separated from dye solution by centrifugation at 3000 r/min for 10 min. The dye concentration in the supernatant was determined using spectrophotometer (UV-2450, Shimadzu, Kyoto, Japan). The dye uptake (q_e, mg/g) was calculated from the mass balance, as Eq. (1):

$$q_e = \frac{V_I C_I - V_F C_F}{M} \tag{1}$$

where, V_I and V_F (L) are the initial and final (initial plus added acid or alkali solution) volume, respectively, C_I and C_F (mg/L) are the initial and final concentrations of dyes, respectively. M (g) is the mass of protonated sludge.

1.3 Potentiometric titration experiments

The potentiometric titration experiment was carried out with 10 g/L of protonated sludge. Plastic bottles (50 mL) were used for the test. The protonated sludge and 30 mL of CO_2-free water, which was obtained by stripping deionized distilled water with nitrogen gas for 2 h with vigorous mixing, were placed in each bottle. Different volumes of 1 mol/L NaOH or 1 mol/L HNO_3 were added to the protonated sludge suspensions. After closing the bottle caps, the bottles were agitated at 300 r/min, 25°C for 24 h. Preliminary tests revealed that 24 h was a sufficient time to achieve the proton sorption equilibrium. The equilibrium pH was measured using a pH meter (Muti-340i, WTW,

Germany). During the titration experiment, the CO_2-free condition was maintained to avoid any influence of inorganic carbon on the solution pH.

1.4 SEM, FT-IR, and XPS analysis

The morphology of the sludge was studied by scanning electron microscopy (SEM) (FEI, SIRion200, the Netherlands). All specimens were coated with a thin layer of gold under vacuum and the image magnification was 5000×.

Infrared spectra of the protonated sludge were obtained using a Fourier transform infrared spectrometer (FT-IR) (NEXUS-470, Thermo Nicolet, USA) within the range of $400–4000$ cm^{-1} to identify the functional groups of protonated sludge.

The surface composition of the protonated sludge was determined by X-ray photoelectron spectroscopy (XPS) on a VG Multilab 2000 electron spectrometer (Thermo Electron Corporation, USA) with an Mg K_α source (1253.6 eV) at constant analyzer pass energy of 20.0 eV. The binding energy is estimated to be accurate within 0.2 eV. All binding energies (BEs) were corrected referencing to the C 1s (284.6 eV) peak as an internal standard.

2 Results and discussion

2.1 Adsorption performance of RR4 and MB on sludge

2.1.1 Influences of pH

To understand the pH dependence of biosorption, the variation in the adsorption of MB and RR4 by the protonated sludge was studied in the pH range 1–11 and 1–9, respectively. The results are shown in Fig. 1. In the case of MB, as pH increased from 1 to 11, the uptake increased and reached maximum value at pH $\geqslant$ 8.3. However, acid condition favored biosorption of RR4. The RR4 uptake decreased from 18.8 mg/g (pH 1.7) to 0 (pH 6.9) with pH increase.

2.1.2 Adsorption isotherm

Biosorption isotherm for MB and RR4 were obtained under pH 9 and 1, respectively. The initial MB and RR4 concentrations were varied within the ranges of 50–1500 mg/L and 50–1000 mg/L respectively, resulting in different
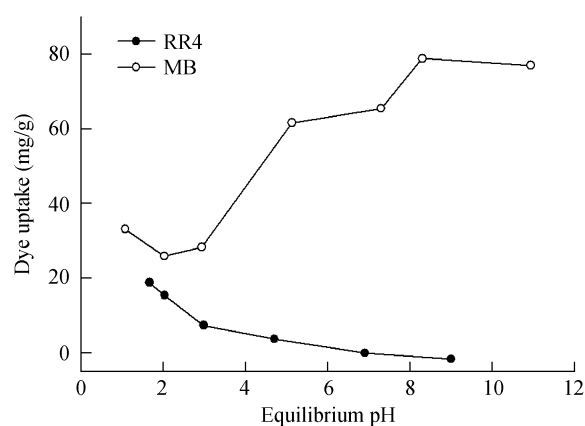

Fig. 1 Effect of pH on the adsorption of MB and RR4 by protonated sludge.

final dye concentrations after sorption equilibrium. The dependencies of the adsorbed amounts of dyes on their equilibrium concentrations are shown in Fig. 2. A steep initial slope with an eventual highest uptake value was observed in these two isotherm curves.

Langmuir (Eq. (2)) and Freundlich (Eq. (3)) adsorption isotherms were used to fit the experimental data.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

where, q_e is the amount of adsorbed dye, C_e is the equilibrium concentration of the dye in solution, q_m is the maximum biosorption capacity and K_L is the Langmuir constant and related to the free energy of biosorption.

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (3)$$

where, K_F and $1/n$ are Freundlich empirical constants, which are dependent on several environmental factors.

The parameters, along with correlation coefficients (R^2) and percentage error values are listed in Table 2. The results indicate that Langmuir isotherm models are well fitted for both dyes in this biosorption system. Comparing with previous studies, the maximum RR4 uptake by protonated sludge (73.7 mg/g at pH 1) was slightly lower than that of *Corynebacterium glutamicum* biomass (q_m = 104.6 mg/g) (Won *et al*., 2005) and higher than that of F-400 (q_m = 13.6 mg/g) (Lim *et al*., 2003). The maximum uptake of MB (235.3 mg/g) was higher than that of activated carbon (q_m = 102.04 mg/g) (Basar, 2006) and fibrous clay minerals (39–85 mg/g) (Yun, 2004).

2.2 SEM image of sludge

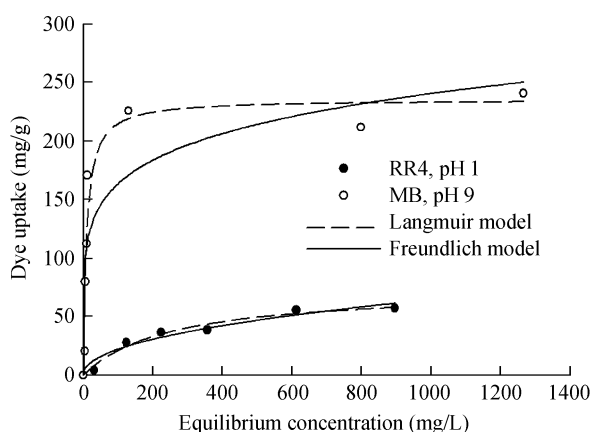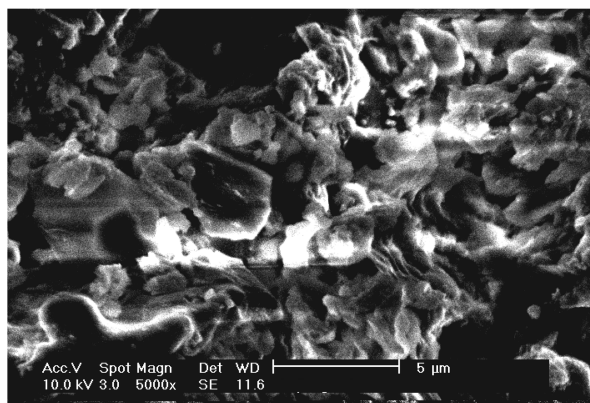As Fig. 3 shown, the sludge particle surface was irregular with highly heterogeneous pores.

Fig. 3 SEM image of the protonated sludge.

2.3 Characterization of binding sites

From potentiometric titration data, the proton uptake as a function of solution pH can be obtained based on the proton-binding model (Yun, 2004; Yun *et al*., 2001). The protonated sludge contains some neutral and/or positively charged groups. The titration curve displays its distinct characteristics depending upon the type and amount of the functional groups present (Fig. 4).

Assuming a certain neutral group (BH^i), its reaction with a proton and its related equilibrium constant (K_H^i) are defined as follows (Yun, 2004).

$$BH^i \longleftrightarrow B^{-i} + H^+ \qquad K_H^i = \frac{C_{B^-}^i \cdot C_{H^+}}{C_{BH}^i} \qquad (4)$$
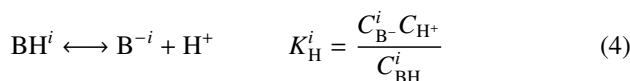
The total concentration of the functional groups is the sum of the protonated and ionized configurations. Therefore, the following Eq. (5) is obtained.

$$C_{B_T}^i = C_{BH}^i + C_{B^-}^i = C_{B^-}^i \times (1 + \frac{C_{H^+}}{K_H^i}) \qquad (5)$$

Fig. 2 Adsorption isotherm of MB and RR4 on the protonated sludge.
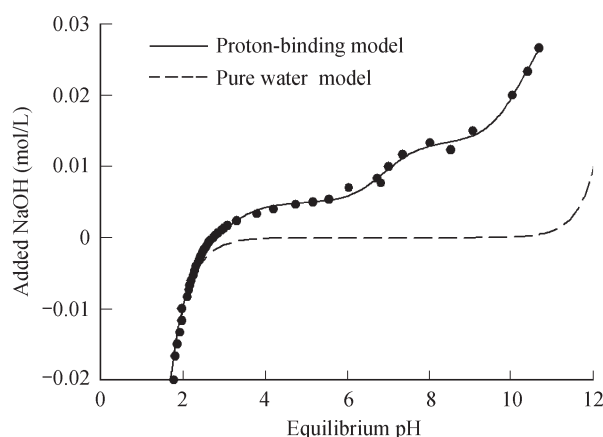

Fig. 4 Potentiometric titration curve of the protonated sludge.

Table 2 Estimated parameters of the Langmuir and Freundlich model

Dye	Langmuir			Freundlich		
	q_m (mg/g)	K_L	R^2	K_F	n	R^2
MB	235.3 ± 19.3	0.1053 ± 0.0342	0.9070	75.74 ± 23.01	5.98 ± 1.86	0.7855
RR4	73.7 ± 7.1	0.0041 ± 0.0011	0.9785	2.6501 ± 1.2992	2.1635 ± 0.3667	0.9527

Data are expressed as mean ± SD.

Consequently, the concentration of the ionized group can be expressed as Eq. (6).

$$C_{B^-}^i = \frac{C_{B_T}^i}{1 + \frac{C_{H^+}}{K_H^i}} \qquad (6)$$

For the titration experiments, the electroneutrality condition must be satisfied. Therefore, Eq. (7) is obtained.

$$C_{Na^+} + C_{H^+} = \sum_{i=1}^{N} C_{B^-}^i + C_{OH^-} \qquad (7)$$

where, $\sum_{i=1}^{N} C_{B^-}^i$ represents a sum of the concentrations of all types (1–N) of ionized groups; C_{Na^+} is identical to the concentration of added hydroxide ions. Combining Eqs. (5)–(7) and yields:

$$C_{Na^+} = \sum_{i=1}^{N} \frac{C_{B_T}^i}{1 + \frac{C_{H^+}}{K_H^i}} + \frac{K_W}{C_{H^+}} - C_{H^+} \qquad (8)$$

where, C_{BT}^i (mmol) is the quantity of the specific function groups in the solution, K_w is ionization constant of water. The proton-binding model was well fitted to the experimental data (Fig. 4) with a high correlation coefficient ($R^2 = 0.9892$). Thus, the three-site model can describe completely the potentiometric titration data (Fig. 4), whereas two- or four-site functional group models do not fit the data (data not shown). The estimated parameters of the proton-binding model are summarized in Table 3.

The first group ($pK_H = 3.15$) have a similar pK_H value for carboxyl group (B–COO⁻) for biological polymers,

Table 3   Estimated parameters of the proton-binding model

Parameter	Functional groups		
	1st group	2nd group	3rd group
pK_H	3.15 ± 0.15	6.89 ± 0.18	10.25 ± 0.25
b (mmol/g)	0.49 ± 0.05	0.85 ± 0.09	1.74 ± 0.35

The coefficient of determination was 0.9892. Data are expressed as mean ± SD.
The 1st group is considered as carboxyl site; 2nd group is possibly phosphonate site; 3rd group is primary amine site.
pK_H represents the dissociation constants of the functional groups. The b values are the numbers of the functional groups.

within a range 3.0–5.0 (Yun and Volesky, 2003; Hajjaji et al., 2006; Karcher et al., 2001). The pK_H value of the second binding site was estimated to be 6.89. This was believed to be phosphonate groups (B-HPO₄⁻), because the phosphonate groups in phospholipids present in the plasma biomass membrane and sludge biomass have a similar pK_H range (Won et al., 2006). The last group has a pK_H value of 10.25, suggesting that is an amine group (B–NH₃⁺) which has a pK_H value range 8–10 for various biomaterials (Hajjaji et al., 2006).

In order to confirm the existence of amine, phosphonate and carboxyl groups in the sludge, FT-IR study was carried out. As shown in Fig. 5a, the FT-IR spectrum displays a number of absorption peaks, indicating the complex nature of the sludge. The FT-IR spectrum shows the characteristic symmetrical as well as asymmetrical stretching vibration absorption peaks of the carboxylic (–OH, C=O), phosphonate (P=O, P–OH, P–O–C) and amine (C–N, N–H) groups, confirming the presences of these functional groups in the protonated sludge (Ashkenazy et al., 1997; Yee et al., 2004).

In order to obtain further insights into the components of the sludge, XPS analysis was conducted as shown in Fig. 5b. The contents of C, O, N, P, and S of the sludge surface were analyzed, which confirm the presence of amine, carboxyl and phosphonate groups in the protonated sludge.

2.4 Mechanism of biosorption

The SEM image showed the rough and highly heterogeneous porous structures of protonated coke. As a myriad of functional groups is often present on the biomass surface, various sorption mechanism including ion exchange, chelation, microprecipitation and complexation may be involved in the sorption process.

Based on their chemical structure, RR4 has four sulfonate groups that have negative charges, while MB is easily dissociated and become positively charged in aqueous solution. The negatively charged sites of the protonated sludge such as carboxyl and phosphonate groups are believed to be the binding sites for MB. Amine group, which are positively charged, are likely responsible for RR4 adsorption. As the solution pH increase, the negatively
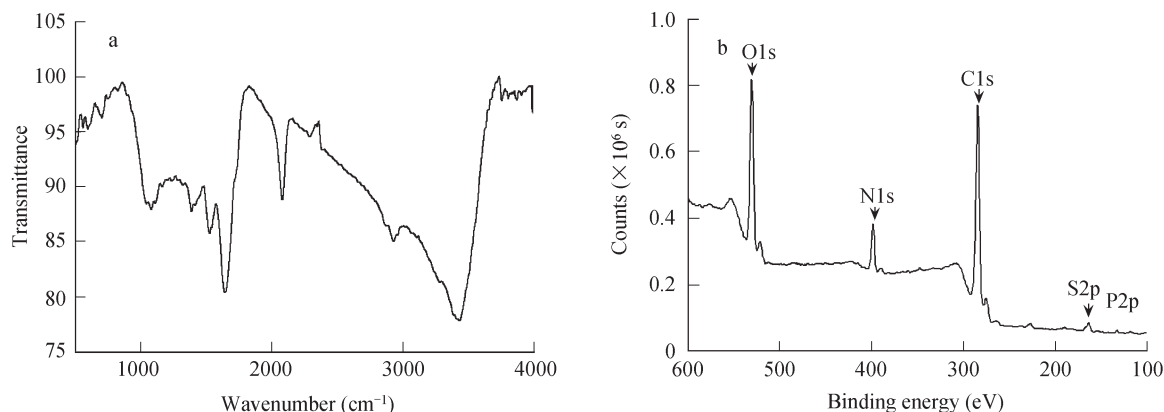

Fig. 5   FT-IR (a) and XPS (b) spectra of the protonated sludge.

charged carboxylate and phosphate binding sites became more and the positively charged amine became less, which result in the increase of MB uptake and the decrease of RR4 uptakes.

According to the kinds and numbers of the functional groups on the protonated sludge, the speciation of the biomass as a function of the solution pH was simulated using the biosorption model (Fig. 6). When pH was lower than 2.0, almost all of the binding sites were occupied by protons, and MB binding could not be expected. As the pH increase to 4, the carboxyl groups became negatively charged; accordingly the MB uptake increased rapidly. When pH was higher than 6, the phosphate groups also become negatively charged. Therefore, the MB uptakes still keep on increasing. The amine groups are charged positively when pH less than 10. The RR4 uptakes sharply decreased from pH 5, and became slower until pH increased to 6.8. This is likely due to the repulsion between negatively charged RR4 and carboxylic and phosphatic groups. Thus, the experimental data agree well with the mechanism of adsorption by electrostatic interaction mainly of the reactive dyes onto the protonated sludge.
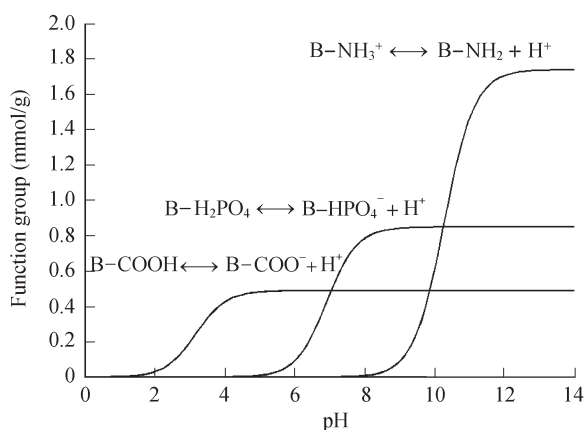

Fig. 6 Speciation of binding sites as a function of the solution pH. The lines were produced by the biosorption model.

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