Journal of Hazardous Materials 189 (2011) 27–33

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Enhancement of acidic dye biosorption capacity on poly(ethylenimine) grafted anaerobic granular sludge

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ARTICLE INFO

Article history:
Received 6 September 2010
Received in revised form
16 December 2010
Accepted 6 January 2011
Available online 15 January 2011

Keywords:
Amino groups
Anaerobic granular sludge
Acid dye
Biosorption

ABSTRACT

Developing a novel biosorbent with high capacity is crucial to remove dyes from waters in an efficient way. This study demonstrated that porous anaerobic granular sludge could be grafted with polyethylenimine (PEI), which definitely improved the sorption capacity towards Acid Red 18 (AR18) removal. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) study revealed that the PEI modification introduced a large number of amino groups on the surface of sludge, and the amino groups played an important role in the adsorption of dye molecule. Analysis of sorption data using a Boyd plot confirms the film diffusion was the rate-limiting step. The equilibrium data were well fitted Langmuir model, with a maximum AR18 uptake of 520.52 mg/g. Removal of AR18 decreased with the increasing pH and the maximum color removal was observed at pH 2.0. The sorption energy calculated from Dubinin-Radushkevich isotherm was found to be less than 8 for the biosorption of AR 18, which suggested that the biosorption processes of dye molecule onto modified anaerobic granules could be taken place by physical adsorption. Various thermodynamic parameters, such as ΔG^0, ΔH^0 and ΔS^0, were also calculated, which indicated that the present system was spontaneous and endothermic process.

1. Introduction

Improper treatment and disposal of dye-contaminated wastewaters from textile, dyeing, printing, ink, and related industries have provoked serious environmental concerns all over the world [1,2]. Various physical–chemical processes are extensively used in treatment of the dye-containing wastewater, which include chemical coagulation/flocculation, precipitation, oxidation, photocatalytic processes and membrane separation [3–5]. Among these technologies, biosorption is receiving increasing attention for the removal of dyestuff from contaminated effluents [6]. A number of biomaterials have been used in the literature, including fungus, sludge, yeast, algae [7–11]. Although these biosorbents are effective for dye removal, they are normally in the form of suspended biomass and have to be separated from the treated effluent or loaded into porous materials for fixed-bed adsorption in actual application.

Microbial granules as the aggregates of self-immobilized bacteria are found to be good biosorbents because of their porous structure and excellent settling properties [12,13]. Gan and Wang evaluated the effects of pH and temperature on biosorption of chlorophenols onto anaerobic granular sludge. [14]. An et al. analyzed performance of mesophilic anaerobic granules for removal of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) from aqueous solution [15]. However, there is little information on enhancing the biosorption capacity of porous anaerobic granules by surface modification.

In our previous research, the anaerobic granule has superior adsorption capacities on basic dye, but it is inefficient for acid dyes removal [13]. Thus increasing the sorption capacity towards acid dyes is prerequisite for the applications of anaerobic granules in practice. As sorption mainly takes place on the biomass surface, increasing/activating the binding sites on the surface would be an effective approach for enhancing the biosorption capacity. Previous study stated that amino groups are the major binding sites in the biosorption of acid dye [16]. Thus, the necessity to increase the coverage of amino groups in an effective way is great. Polyethylenimine (PEI) which is composed of a large number of primary and secondary amine groups in a molecule, exhibits good sorption ability when they are adsorbed or cross-linked on the sorbent surface. Sun et al. reported that aerobic granules exhibited excellent performance on metal ions adsorption, and after grafting with PEI, the adsorption capacity of aerobic granules could be definitely enhanced [17–19]. Compared with the aerobic granules, a mount of gas could be produced inside the anaerobic granules and trans-

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doi:10.1016/j.jhazmat.2011.01.028

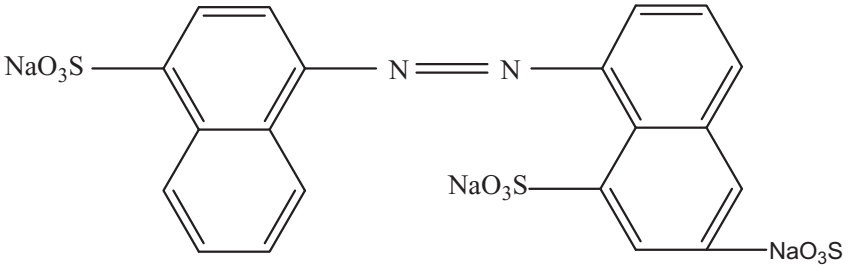


Fig. 1. Chemical structure of AR 18.

port from the core to the granule surface, which results in a more porous structure.

Thus the objective of this study was to investigate the feasibility of modifying anaerobic granular sludge with PEI. We report on Acid Red 18 (AR18), a representative of acid dye removal by modified anaerobic granules, obtaining detailed studies by using different spectroscopic techniques. The presence of many side chains of PEI on the sorbent surface provided a high number of binding sites for acid dyes and, thus enhanced the sorption ability. The sorption behavior and mechanism were also evaluated in detail.

2. Methods

2.1. Materials

The anaerobic granular sludge used in this study was collected from Shandong Meiquan Environmental Protection Technology Ltd., China, which was used for treating starch wastewater. PEI, glutaraldehyde (50% aqueous solution) were purchased from Sigma–Aldrich Company. The dye used in all the experiments was AR18 (C.I. 16255, 50–60% dye content), an acid (anionic) dye, which was obtained from Tianjin Chemical Co., China. Its molecular structure is shown in Fig. 1.

2.2. Biomass preparation and modification

Anaerobic granular sludge was stored in a sealed container at 4 °C until surface modification experiments. Pristine granular sludge was firstly washed with copious amount of deionised water. Then, the washed anaerobic granular sludge was subjected to surface modification. 20 g of pristine granular sludge were added to 0.1 L of 10% (w/v) PEI/methanol solution in a 0.25 L conical flask. The flask was agitated at 140 rpm and 30 °C for 24 h. The biomass was subsequently filtered and washed with methanol to remove residual and unreacted PEI. The biomass was transferred into a 0.25 L conical flask containing 0.1 L of 1.0% (v/v) aqueous glutaraldehyde for cross-linking. The flask was agitated at 140 rpm and 30 °C for 20 min. The modified biomass was washed with deionised water. The mean particle size of modified anaerobic granules was about 1.4 mm.

2.3. Characterization of the biosorbent

2.3.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the pristine and modified anaerobic granular sludge were obtained by using a FT-IR spectrophotometer (Vector 22, Germany). Before the analysis, the wet samples were freeze-dried. Each lyophilized sample was placed on a gold mirror and determined using reflection mode in the wave number range of 400–4000 cm^{-1}.

2.3.2. X-ray photoelectron spectroscopy (XPS)

The chemical composition of the surfaces of the pristine and modified freeze-dried biomass was determined using XPS (PHI 5300, USA) with an Al KR X-ray source (1486.72 eV of photons). The X-ray source was run at a reduced power of 150 W, and the pressure in the analysis chamber was maintained at less than 10^{-8} Torr during each measurement. All binding energies were referenced to the neutral C1 s peak at 284.6 eV to compensate for the surface charging effects. The software package, XPS peak 4.1, was used to fit the XPS spectra peaks, and the full-width at half maximum (FWHM) was maintained at 1.4 for all components in a particular spectrum.

2.4. Sorption experiment

The biosorption of AR18 on modified anaerobic granular sludge was investigated in batch biosorption equilibrium experiments. To determine biosorbent dose, varying amounts of biomass (0.2, 0.4, 0.6, 0.8 and 1.0 g) were used in the adsorption medium and the initial dye concentration was 100 mg/L 0.1 L AR18 solution, which were maintained on a incubated rotary shaker at 160 rpm, 25 °C and pH 4.0. The effect of pH on the biosorption capacity of the biosorbent was investigated in the pH range from 2 to11, and the 100 mg/L 0.1 L AR18 solution, which were maintained on a incubated rotary shaker at 160 rpm and 25 °C. The effect of contact time and initial dye concentration on the biosorption was studied by agitating 8.0 g modified anaerobic granular sludge in a series of beaker containing 2 L AR18 solution of known concentration (50, 100 and 250 mg/L), 2 mL samples were taken at suitable time intervals.

Biosorption equilibrium studies were carried out by adding 0.4 g of modified anaerobic granular sludge in a series of 0.25 L flasks containing 0.1 L AR18 solution of different dye concentrations at three different temperatures (25, 35 and 50 °C).

In order to assess the practical utility of the adsorbent, desorption experiments were conducted. 0.4 g modified anaerobic granular sludge with adsorbed AR18 was treated by 0.5 M HCl for a predetermined time.

The concentration of AR18 remaining in solution was measured colorimetrically using a spectrophotometer (UV-754, Shanghai, China) at a maximum wavelength of 510 nm. All the samples were filtered through 0.45 μm membranes before measure.

3. Results and discussion

3.1. Characterization of the modified anaerobic granular sludge

The effect of chemical modification on the adsorption capacity was presented in Fig. 2. After modified with PEI, the sorption capacity of anaerobic granular sludge towards AR18 was significantly improved, because new amine groups were introduced on the anaerobic granular sludge surface, which play an important role in the acid dye adsorption.

After modification, the atomic ratio of C:N:O turns to 72.29:9.32:16.21 from 71.6:4.69:23.71. The more significant

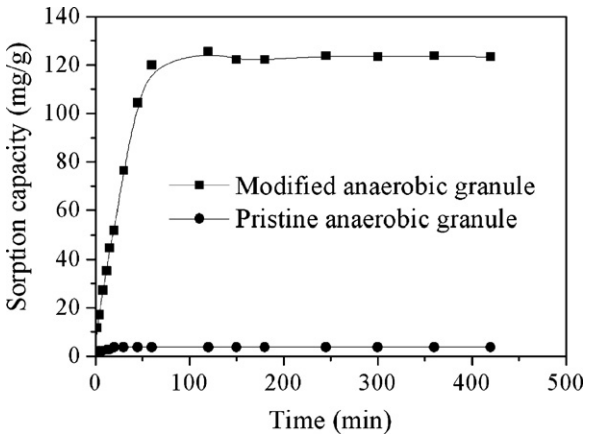


Fig. 2. Effect of chemical modification on the adsorption capacity, initial concentration 100 mg/L.

increase in nitrogen and decrease in oxygen on the modified anaerobic granules may be attributed to crosslinking reaction with PEI molecules (Scheme 1). Fig. 3a and b shows the N1s spectrum of pristine and modified anaerobic granular sludge, the binding energy at 399.8 eV can be assigned to nitrogen in the NH (NH_2)/CN [20]. The new binding energies at 398.6 eV can be assigned to the N in the tertiary amine groups (>N–), indicating that aldehyde groups of glutaraldehyde were reacted with amine groups of biomass and PEI. Thus, the glutaraldehyde actually serves as a bridge to graft the PEI onto the biomass surface. In the O 1s spectrum (Fig. 3c and d), the binding energy at 531.8 and 532.7 eV can be assigned to the O in the C=O and alcoholic C–O groups [21]. In Fig. 3d, the peak at the binding energy of 532.7 eV has increased, which may be due to the formation of new hydroxyl groups during crosslinked with glutaraldehyde. As more amine groups were introduced on the surface of the anaerobic granular sludge, the electrostatic attraction between amine groups and sulfonate groups of AR18 make the dye molecule adsorption on the anaerobic granule surface, which is responsible for the improvement of the sorption capacity.

3.2. Effect of pH

The pH is an important parameter that affects dye sorption; it could influence the properties of the sorbent as well as sorbate speciation. Fig. 4 shows the uptake of AR18 was increased as the pH decreased, and the optimum pH value for AR18 was determined to be 2.0.

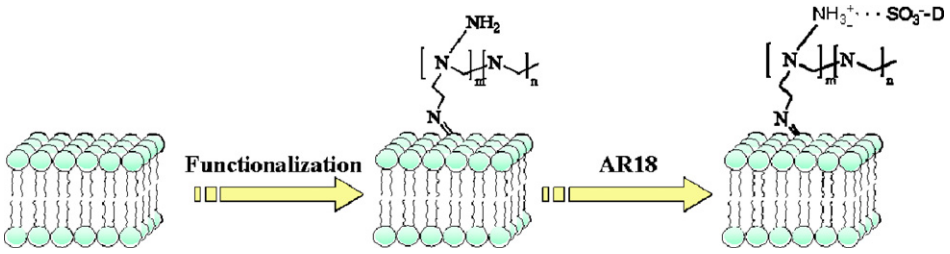
In the aqueous solution, AR18 is first dissolved and the sulfonate groups of AR18 (D-SO_3Na) are dissociated and converted to anionic dye ions [21]

$$\text{D-SO}_3\text{Na} \xrightarrow{\text{H}_2\text{O}} \text{D-SO}_3^- + \text{Na}^+ \quad (1)$$

In the presence of H^+, the amino groups of modified anaerobic granular sludge become protonated.

$$\text{Biomass-NH}_2 + \text{H}^+ \rightleftharpoons \text{Biomass-NH}_3^+ \quad (2)$$

The biosorption process may be due to the electrostatic attractions between negatively charged dye anions and positively charged cell surface. Hydrogen ion also acts as a bridging ligand



Scheme 1. (a) Functionalization of the anaerobic granular sludge and (b) adsorption of AR18 on the MAGS.

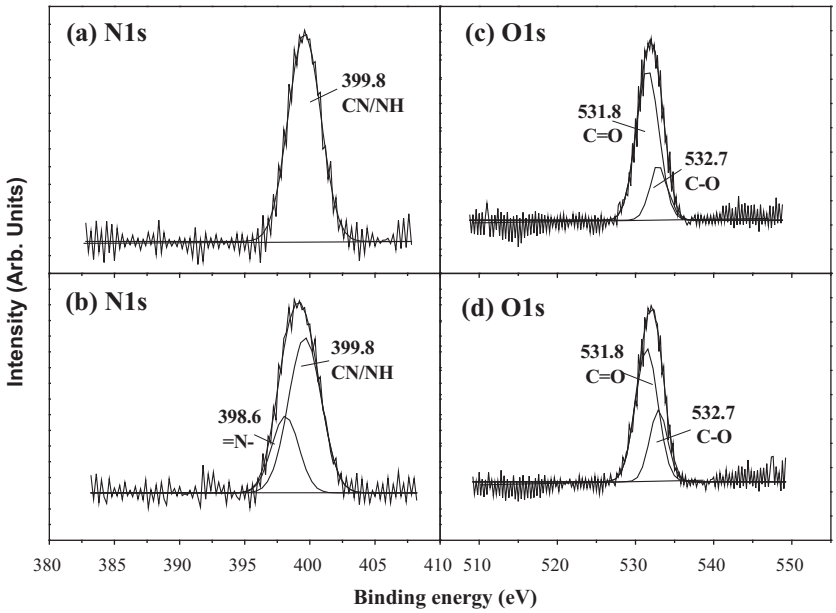


Fig. 3. XPS O1s and N1s spectra of the pristine biomass (a and c) and PEI-modified biomass (b and d).

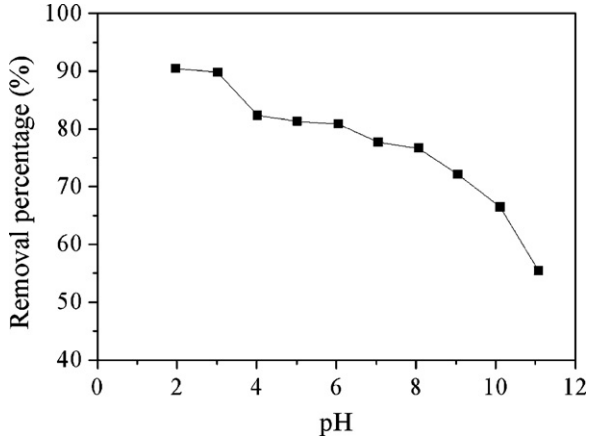


Fig. 4. Effect of pH on the removal percentage of AR 18.

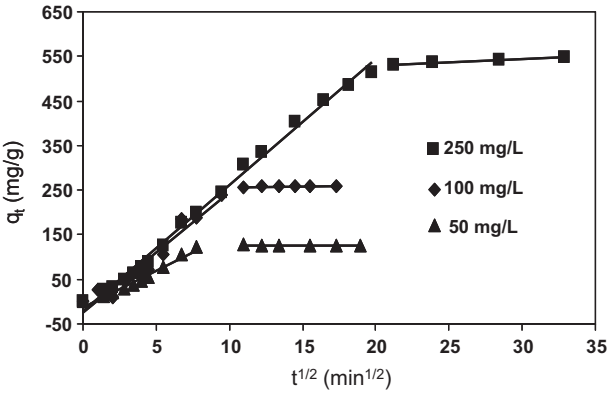


Fig. 5. Intraparticle diffusion kinetics for adsorption of AR 18.

between modified anaerobic granular sludge and dye molecule [22].

$$\text{Biomass-NH}_3^+ + \text{D-SO}_3^- \rightleftharpoons \text{Biomass-NH}_3^+\text{O}_3\text{S-D} \quad (3)$$

With increase in the system pH, the number of positively charges on the biosorbent surface decreases. The electrostatic attractions between the positively charged surface of modified anaerobic granules and the negatively charged dye molecule will decrease. The amount of adsorption decreased with increasing of pH. Therefore, the interaction between dye molecules and biosorbent is basically a combined result of charges on dye molecules and the surface of the biosorbent (Scheme 1).

3.3. Biosorption kinetics and modeling

Biosoption kinetics of AR18 at different initial concentrations were studied to determine the equilibrium times (Fig. S2). The result indicated that the adsorption is rapid in the initial stages and gradually decreases with progress of adsorption. The rapid uptake of the dye in the initial stages indicates that the sorption process could be ionic in nature where the acid dye molecules bind to the various positive charged organic functional groups present of the surface of the biomass [23]. The equilibrium time was found to be 60, 120 and 450 min for 50, 100 and 250 mg/L of dye, respectively. Therefore, equilibrium time was set conservatively at 2 h for further experiments.

3.3.1. The first- and second-order kinetic model

The biosorption kinetics were investigated using two classical kinetics models, the pseudo-first-order and pseudo-second-order kinetic model.

The sorption uptake kinetics for AR18 by modified anaerobic granular sludge were analyzed by non-linear curve fitting analysis method, using Microcal (TM) Origin software. And the parameters were tabulated in Table 1.

It was observed that the values of initial adsorption rates $h = K_2 q_e^2$ increased with an increase in the initial dye concentration. It could be attributed to the increase in the driving force for the mass transfer, allowing more dye molecules to reach the surface of the adsorbents in a shorter period of time. The results showed that the pseudo-first-order model fitted the simulation curve much better than the pseudo-second-order model.

3.3.2. Rate-determining step

To interpret the experimental data, it is necessary to identify the steps involved during adsorption, described by external mass transfer (film diffusion) and intraparticle diffusion.

Fig. 5 shows the modeling result of AR18 sorption on the modified anaerobic granular sludge using the intraparticle diffusion model. The plots were linear and did not pass the origin, indicating the significance of intraparticle diffusion existed in the biosorption of dyes onto modified anaerobic granular sludge. From Fig. 5, it was noted that the linear portion ended with a smooth curve followed by a linear portion. A similar type of pattern was reported previously by Sankar et al. for acid and direct dye onto rice bran-activated carbon and also by Sivaraj et al. for acid violet onto orange peel [24,25]. The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by external mass transfer and intraparticle diffusion. The initial curved portion of the plot indicates a boundary layer effect while the second linear portion is due to intraparticle or pore diffusion. The values of intraparticle diffusion rate constant, k_i, calculated are shown in Table 1. The results indicated that intraparticle diffusion rate increases with increasing initial dye concentration in solution. An increase in initial concen-

Table 1
Kinetic parameters obtained from the various models.

Initial concentration C_0 (mg/L)	Experimental q_{ex} (mg/g)	Pseudo-first order rate constants			Pseudo-second order rate constants			
		q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg min)	h (mg/g min)	R^2
50	126.08	127.80	0.0329	0.9889	144.33	0.00027	5.624	0.9673
100	259.27	267.01	0.0208	0.9867	325.82	0.00007	7.431	0.9735
250	544.13	542.08	0.0071	0.9946	645.19	0.00003	12.49	0.9945

Initial concentration C_0 (mg/L)	Film diffusion constants		Intraparticle diffusion constants	
	k_s (1/min)	R^2	k_i (mg/g $min^{1/2}$)	R^2
50	0.0156	0.9788	0.0109	0.9327
100	0.0107	0.9462	0.4679	0.6048
250	0.0023	0.929	1.3844	0.9316

Table 2
Isotherm constants obtained from Langmuir and Freundlich model.

T (°C)	Langmuir			Freundlich			Dubinin-Radushkevich			
	Q^0 (mg/g)	B (L/mg)	R^2	K_F	$1/n$	R^2	q_m	β	R^2	E
20	418.38	0.1049	0.9938	128.85	0.2341	0.9709	321.79	2×10^{-6}	0.9832	0.87
30	423.29	0.2643	0.9977	216.24	0.1555	0.6949	348.28	8×10^{-7}	0.9712	1.37
50	520.52	0.3599	0.9925	222.70	0.2063	0.9825	461.19	1×10^{-7}	0.9642	3.88

tration will produce a higher concentration gradient which will eventually cause faster diffusion and quicker biosorption.

As the double nature of intraparticle diffusion plot confirms the presence of both film and pore diffusion, in order to predict the actual slow step involved, the kinetic data were further analyzed using the Boyd kinetic expression.

The Boyd plot is obtained by plotting Bt versus time t. The Bt is expressed by the following equation:

$$Bt = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \quad (4)$$

The linearity of the plot is employed to distinguish between external-transport-(film diffusion) and intraparticle-transport-controlled rates of sorption [26]. A straight line passing through the origin is indicative of sorption processes governed by particle-diffusion mechanisms; otherwise they are governed by film diffusion [27]. In our case, the plots were neither linear nor passed through the origin (data not shown). This indicates that film diffusion is the rate-limiting sorption process.

3.4. Adsorption isotherms

3.4.1. The Langmuir and Freundlich isotherm

Biosorption isotherms are important for the description of how biosorbate will interact with a biosorbent and are critical in optimizing the use of biosorbent. In order to investigate the biosorption isotherm, two equilibrium models, the Langmuir and Freundlich isotherm models, were analyzed.

The non-linear adsorption isotherm constants obtained at three different temperatures are given in Table 2. It was observed that the equilibrium adsorption data were very well presented by Langmuir isotherms. It confirmed the monolayer adsorption process of AR18 onto modified anaerobic granular sludge [28]. The biosorption capacity of modified anaerobic granular sludge obtained from Langmuir isotherm equation for AR18 in this study was found to be moderately higher than that of many biosorbents reported in the literature (Table 3).

The dimensionless adsorption intensity (R_L) is calculated using the following formula:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

The values of R_L for C_0 = 100 mg/L obtained were found to be less than 1 for dye molecule adsorption on modified anaerobic granular sludge. It confirmed that the adsorption process is favorable. In other words, modified anaerobic granular sludge is a suitable biosorbent for AR18.

3.4.2. The Dubinin-Radushkevich isotherm

The equilibrium data were also subjected to the D–R isotherm model to determine the nature of biosorption processes as physical or chemical. The D–R sorption isotherm is more general than Langmuir isotherm, as its derivation is not based on ideal assumptions such as equipotent of the sorption sites, absence of steric hindrance between sorbed and incoming particles and surface homogeneity on microscopic level [32]. The linear presentation of the D–R isotherm equation is expressed by SarI and Tuzen [33]:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (6)$$

where β is the activity coefficient related to biosorption mean free energy (mg^2/J^2) and ε is the Polanyi potential ($\varepsilon = RT \ln(1 + 1/C_e)$).

The constant β giving an idea about the mean free energy E (kJ/mg) of biosorption can be calculated using the following relationship:

$$E = \frac{1}{(2\beta)^{1/2}} \quad (7)$$

where E values give the information about biosorption mechanism as chemical ion-exchange or physical adsorption. If it lies between 8 and 16 kJ/mol, the adsorption process takes place chemically and while $E < 8$ kJ/mol, the adsorption process proceeds physically [34]. The values of E were found to be less than 8 for the biosorption of AR 18. These results suggest that the biosorption processes of dye molecule onto modified anaerobic granules could be taken place by physical adsorption.

3.5. Thermodynamic of biosorption

To estimate the effect of temperature on the biosorption of AR18 onto modified anaerobic granular sludge, the free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were determined. Thermodynamic parameters can be calculated from the variation of thermodynamic equilibrium constant K_0 with the change in temperature.

The thermodynamic parameters are listed in Table 4. The negative ΔG^0 values indicated thermodynamically feasible and spontaneous nature of the biosorption. The ΔH^0 was found to be

Table 3
Comparison of the uptake capacities of acid dyes for various adsorbents.

Dyes	Adsorbents	Q^0 (mg/g)	T (°C)	References
Acid Red 337	*Enteromorpha prolifera*	210.87	30	[29]
Acid Blue 324	*Enteromorpha prolifera*	160.59	25	[29]
Acid Blue 15	*Azolla rongpong*	76.34	30	[30]
Acid Green 3	*Azolla rongpong*	83.33	30	[30]
Acid Red 88	*Azolla rongpong*	81.30	30	[30]
Acid Orange 7	*Azolla rongpong*	76.92	30	[31]
Acid Red 18	*nanochitosan*	334.42	25	[31]
Acid Blue 290	*Spirogyra rhizopus*	135.60	30	[8]
Acid Blue 324	*Spirogyra rhizopus*	367.00	25	[8]
Acid Red 18	Modified anaerobic granule	418.38	20	This work

Table 4
Thermodynamic parameters of AR18 biosorption on modification anaerobic granular sludge.

T (°C)	K_0	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	$\Delta S^0 \times 10^{-3}$ (kJ/mol)
20	1.504	−2.6639	1.236	0.01331
35	1.866	−4.7791		0.01953
50	1.257	−2.9126		0.01284

1.236 kJ/mol for AR 18, indicated the endothermic nature. Positive values of ΔS^0 suggested good affinity of the dye towards the adsorbent [17].

3.6. Desorption studies

Repeated availability is an important factor for an adsorbent. Such adsorbent should not only possess higher adsorption capability, but also show better desorption, which will significantly reduce the overall cost for adsorbent. Desorption tests were carried out by 0.5 M HCl (Fig. 6). In the consecutive cycles sorption–desorption experiments, adsorbent desorbed with 0.5 M HCl has good efficiency in removal of AR18 from solution. During the desorption process with HCl solution, the amino groups of modified anaerobic granular sludge were protonated, improved the active sites. However, with increasing sorption–desorption cycles, the loss of biosorption capacity increased, which can be associated with interactions between the complexing agent and the functional groups or active sites of the biomass. It is expected that these sites were blocked in an irreversible way by dyes already adsorbed in the previous cycle. Thus the capacity of modified anaerobic granule was firstly increased, and then decreased.

3.7. FTIR analysis

FTIR spectra of raw and modified anaerobic granules were recorded to obtain information on the chemical functionalization of the adsorbent surface. The main absorption bands for pristine granular, as depicted in Fig. 7, were found at 3417, 2923, 1653, 1541, 1391, and 1050 cm^{-1}. The broad and strong band ranging from 3600 to 3200 cm^{-1} may be due to the overlapping of OH and NH stretching [18,35]. The region between 3000 and 2800 cm^{-1} exhibited the C–H stretching vibrations of $-CH_3$ and $>CH_2$ functional groups attributed to fatty acid found in membrane phospholipids [36]. At 1391 cm^{-1}, it was a characteristic peak of symmetric vibrational COO– frequencies of terminal amino acid on biomass [18]. The spectrum presents some changes after the granular sludge was modified with PEI. In Fig. 6b, the broad overlapping peak shifts from 3417 to 3424 cm^{-1} because a large number of amine groups were

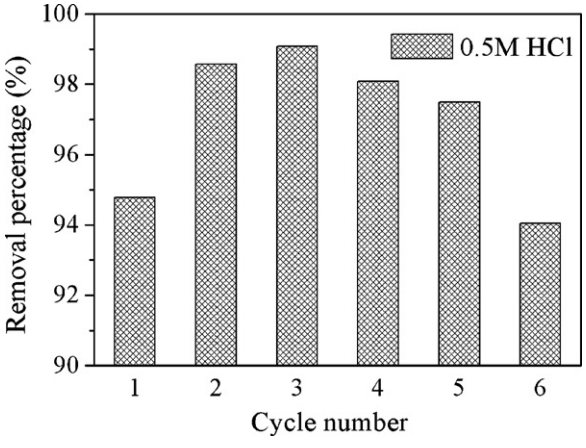


Fig. 6. Adsorption capacities of modified anaerobic granules for AR 18 dye in six successive sorption–regeneration cycles.

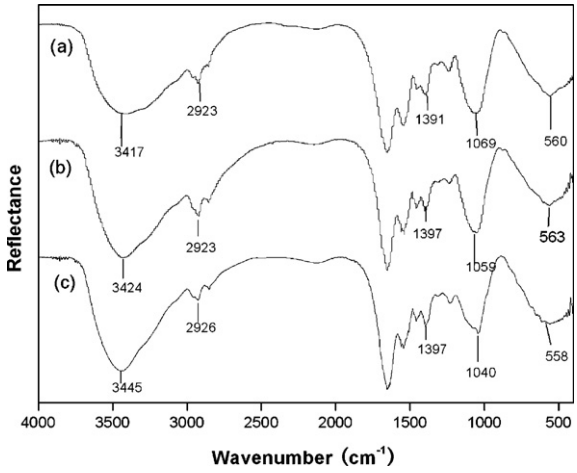


Fig. 7. FTIR spectra of: (a) pristine anaerobic granular sludge, (b) modified anaerobic granular sludge, and (c) dye loaded modification anaerobic granular sludge.

introduced on the surface [37], and a number of hydroxyl groups were formed during crosslinked with glutaraldehyde [38].

Fig. 7c shows the changes in the spectrum of the biomass after sorption of dye molecule. The broad overlapping region for N–H and O–H stretching in range of 3600–3200 cm^{-1} shifted to lower wave number 3417 cm^{-1}. According to the previous study, the broad and strong and ranging from 3200 to 3600 cm^{-1} may be due to the overlapping of –OH and –NH stretching, however, the strong broad band at the wavenumber region of 3300–3500 cm^{-1} is characteristic of the –NH stretching vibration [19]. Similarly, the peak at 1543 cm^{-1} attributed to N–H bending shifts to the higher peak at 1548 cm^{-1} after dye uptake. These changes are attributed to the interactions of amino groups on the modified anaerobic granular sludge and the colored dye ions. In addition, the peaks at 1239 m^{-1}, which is characteristic of S=O stretching [39], was shifted to 1232. It means the increase of the S=O groups, the structural formulae of AR18 in this study show the presence of the sulfonic acid groups which has an S=O functional group.

4. Conclusions

Modified anaerobic granular sludge has much better adsorption capacity for AR18 than pristine sludge. XPS and FTIR study revealed that the PEI modification introduced a large number of amino groups on the surface of anaerobic granular sludge. And the amino groups played an important role in the adsorption of dye molecule.

The dye removal decreased with the increasing of pH and the maximum color removal was observed at pH 2.0. Sorption data were found to follow pseudo-first-order kinetic model and q_e at initial concentration 100 mg/ml was 267.01 mg/g. Analysis of sorption data using a Boyd plot confirms the film diffusion was the rate-limiting step for the dye concentration ranges in the present investigation. The equilibrium data were analyzed using Langmuir and Freundlich model, and well fitted Langmuir model. The negative values of ΔG^0 and ΔS^0 suggested that the interaction of AR18 adsorbed by modified anaerobic granular sludge was spontaneous. $\Delta H^0 > 0$ suggests the biosorption is endothermic reaction.

0.5 M HCl solution has good potential to dissolve by batch desorption technique, which maintaining the conditions similar to batch adsorption studies. FTIR analysis revealed the interaction of amino groups on the modified anaerobic granular sludge and the colored dye ions. The modified anaerobic granular sludge prepared in this study has a promising application in water and wastewater treatment for acid dyes removal.

Acknowledgments

The authors wish to thank the National Natural Science Foundation of China (No. 50978157), the National High-Tech R&P Program (863) of China (2008AA06Z301) and the Shanghai Tongji Gao Tingyao Environmental Science & Technology Development Foundation for the partial support of this study.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.01.028.

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