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Biosorption of Acid Yellow 17 from aqueous solution by non-living aerobic granular sludge

Jingfeng Gao*, Qian Zhang, Kai Su, Ranni Chen, Yongzhen Peng

College of Environmental and Energy Engineering, Beijing University of Technology, 100 Pingleyuan, Chaoyang District, Beijing 100124, China

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ABSTRACT

Batch biosorption experiments were carried out for the removal of Acid Yellow 17 from aqueous solution using non-living aerobic granular sludge as an effective biosorbent. The effects of solution pH value, biosorbent dosage, initial Acid Yellow 17 concentration, NaCl concentration and temperature on the biosorption were investigated. The experimental results indicate that this process was highly dependent on pH value and the pH value of 2.0 was favorable. The Temkin isotherm was more applicable for describing the biosorption equilibrium at the whole concentration range than the Freundlich and Langmuir isotherm. The results of kinetics study show that the pseudo-second-order model fitted to the experimental data well. Both intraparticle diffusion and boundary layer diffusion might affect the biosorption rate. Thermodynamic studies demonstrate that the biosorption process was spontaneous and exothermic. The FTIR analysis before and after Acid Yellow 17 binding indicated that functional groups such as amine, hydroxyl, carboxyl and either on the non-living aerobic granular sludge would be the active binding sites for the biosorption of the studied dye. These results show that non-living aerobic granular sludge could be effectively used as a low-cost and alternative biosorbent for the removal of Acid Yellow 17 dye from wastewater.

1. Introduction

There are estimated 7×10^5 to 1×10^6 tons dyes that are produced annually in the world [1], and China's dyestuff production reached a total of 7.537×10^5 tons in 2007 [2], China has become the largest synthetic dyes producing country. Most of the dyes are used in textile processing, in which the degree of fixation of dyes to fabrics is never complete, and 10–15% of the used dyes enter the environment through wastes, resulting in dye-containing effluents [1]. If the effluents are not properly treated, these dyes may pose aesthetic problem for the presence of dyes even at a very low concentration and reduce photosynthetic action within ecosystem, also their breakdown products may be toxic and even carcinogenic to aquatic life [3,4]. It is known that dyes are stable to light, heat and oxidizing agents, and are usually biologically non-degradable [1,3,4].

Of the dyes, water soluble reactive and acid dyes are the most problematic, as they tend to pass through conventional treatment systems unaffected, hence, their removal is also of great importance [3]. Acid Yellow 17 (AY 17), a monoazo dye, is widely used in dyeing wool, silk, cotton, leather, paper and hot stamping foil. Also it is a common additive found in ordinary household products such as shampoo, bubble bath, shower gel, liquid soap, multi-purpose cleanser, dishwashing liquid and alcohol-based perfumes [5]. Many governments have established strict environmental regulations associated with dyestuffs, which require associated industries to find economically viable wastewater treatment methods.

During the past years, a number of wastewater treatment methods have been reported and attempted for the removal of pollutants from dye-containing wastewaters, such as coagulation and flocculation, adsorption, membrane separation and advanced oxidation [6]. Most of the techniques may be efficient for the removal of dyestuffs, but their initial and operational costs are so high that they cannot be widely applied on a large scale in some industries, especially in developing countries. Among various methods adsorption occupies a prominent place in dye removal, which can be defined as a process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings [1]. Although the removal of azo dyes through activated carbon adsorption is highly effective, its use is limited due to the high cost of activated carbon and 10–15% loss during regeneration. Therefore, low-cost, renewable, locally available and efficient alternative adsorbents are required. A wide range of waste materials have been used for this purpose, including bottom ash [7–9], de-oiled soya [8–10], waste carbon slurries [11–13], blast furnace slag [12], peat [14], bagasse fly ash [15], baker's yeast [16], activated sludge [17], etc. As a typical kind

* Corresponding author. Tel.: +86 10 67396047; fax: +86 10 67391983.
E-mail addresses: gao.jingfeng@bjut.edu.cn, gao158@gmail.com (J. Gao), zq08@emails.bjut.edu.cn (Q. Zhang), sukaidido@emails.bjut.edu.cn (K. Su), serryranni@emails.bjut.edu.cn (R. Chen), pyz@bjut.edu.cn (Y. Peng).

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of the low-cost adsorption, biosorption can be defined as the passive uptake of organic and inorganic species including metals, dyes and odour causing substances by dead/inactive biological materials or by materials derived from biological sources [18]. The biological materials may be bacteria, fungi, algae, industrial wastes, agricultural wastes and other polysaccharide materials [18]. As compared with bioaccumulation, biosorption is a metabolism-independent processes, there is no requirement for the supplement with any nutrients for maintaining growth of non-living biomass [19].

The activated sludge process has been used worldwide in municipal and industrial wastewater treatment. In the EU as a whole, for example, annual waste sludge production exceeds 10 millions tons (dry weight) [20]. In China, sewage sludge produced can be estimated to be 3.5 million tons (dry weight) in 2005 [21]. Due to low-cost, free availability and high biosorption capacity, perhaps activated sludge is the most abundant source of new biosorption materials [22]. However, like most biosorbents, activated sludge are in the form of dispersed microorganisms, which are small particle size, low density, poor mechanical strength and little rigidity, causes practical difficulties in solid–liquid separation and biomass regeneration, and limits their applications under real conditions [22]. The immobilized types of biosorbents can overcome these drawbacks, but the employment of immobilization procedures is expensive and complex [23].

To date, as self-immobilized microbial aggregates for wastewater treatment, the application of aerobic granular sludge has been regarded as one of the promising processes in wastewater treatment, and was developed for treating high strength wastewaters containing organics, nitrogen, phosphorus, toxic substances and xenobiotics [24]. Several review papers have been published in the last 5 years and they covered almost every aspects of aerobic granulation [24–26]. Compared to conventional activated sludge, aerobic granular sludge has the advantages of excellent settle ability, dense and porosity microbial structure, suggesting that it could satisfy the basic requirements for biosorbents for dyestuffs removal. Unlike anaerobic granulation technology which needs a long cultivation period, aerobic granular sludge could be rapidly cultivated using activated sludge as seed in sequencing batch reactors (SBRs), with a wide variety of feed substrates including glucose, acetate, ethanol, phenol, synthetic wastewater and real wastewater [24]. In a batch system, it could not only be used for pollution control, but also be used as biosorbent for dye removal from industrial wastewater streams. Living aerobic granular sludge had been used as a biosorbent for the removal of heavy metals [23] and Malachite Green (a cationic triphenylmethane dye) [27]. However, there are no literatures concerning biosorption of acid dyes onto non-living aerobic granular sludge.

Aerobic granular sludge contains mainly bacteria, protozoa and extracellular polymeric substances (EPS). The functional groups on bacteria, protozoa and EPS, such as, carboxyl, phosphonate, amine, hydroxyl groups and other components, provide binding sites for dye biosorption [28]. In view of more complicated structures of aerobic granular sludge as compared with freely suspended biomass, the equilibrium, kinetics and mechanism of biosorption using aerobic granular sludge are new and more difficult to establish. However, the often used isotherm model (Langmuir isotherm [29], Freundlich isotherm [30], Temkin isotherm [31], etc.), kinetic model (pseudo-first-order model [32], pseudo-second-order model [33], Weber and Morris model [34], etc.) can borrow the theoretical concepts and provide academic references that may shed light on biosorption behavior using non-living aerobic granular sludge.

Therefore, the main object of this study was to examine the feasibility of using non-living aerobic granular sludge as a novel type of biosorbent for the removal of acid dye from aqueous solution, AY 17 was used as a model compound. Effects of different parameters including pH value, biosorbent dosage, initial dye concentration, NaCl concentration and temperature were studied to optimize the biosorption process. The isotherms, kinetics and thermodynamics were explored to describe the experimental data. Furthermore, the Fourier transform infrared (FTIR) analysis was conducted to investigate the dye interaction with the biomass involved in the AY 17 biosorption process.

2. Materials and methods

2.1. Biosorbents

Aerobic granular sludge used for the biosorption tests was collected from a lab-scale SBR fed with glucose as the sole carbon source. The composition of the synthetic wastewater was as follows (in mg/L): glucose, 583.2; NH_4Cl, 229.3; KH_2PO_4, 43.9; $MgSO_4{\cdot}7H_2O$, 90; $CaCl_2{\cdot}2H_2O$, 14 and trace element solution, 0.4 mL/L. This gave a COD:N:P of 600:60:10. The trace element solution contained (in g/L): $FeCl_3{\cdot}6H_2O$, 1.5; H_3BO_3, 0.15; $CuSO_4{\cdot}5H_2O$, 0.03; KI, 0.18; $MnCl_2{\cdot}H_2O$, 0.12; $Na_2MoO_4{\cdot}2H_2O$, 0.06; $ZnSO_4{\cdot}7H_2O$, 0.12; $CoCl_2{\cdot}6H_2O$, 0.15 and EDTA, 10 [35].

The reactor was operated in successive cycles of 6 h each consisting 2 min of feeding, 330 min of aeration, 6 min of settling, 2 min of effluent withdrawal and 20 min of idle. The temperature of the reactor was maintained at $25 \pm 1\,^{\circ}C$. During the aeration period, the dissolved oxygen concentration was around 6 mg/L.

The mean diameter of the aerobic granular sludge cultivated in the SBR was around 2.0 mm, and the mean settling velocity was 33 m/h. Generally, aerobic granular sludge suffers intense hydraulic or mechanical shear force in the bioreactors. Aerobic granular sludge with a high physical strength could resist the disintegration caused by compression [36] and high shear abrasion [37]. Prior to use, the aerobic granular sludge was first washed with distilled water three times to remove the surface soluble ions. Fig. 1 shows the images of aerobic granular sludge. In order to inactivate the organisms, aerobic granular sludge were dried at 105 °C for 2 h. As seen from Fig. 1(a and b), this method did not affect the aerobic granular sludge's physical integrity. When non-living aerobic granular sludge were immersed in distilled water at room temperature (Fig. 1(c)), they rapidly recovered their morphology in 1 min; after the non-living aerobic granular sludge contacted with the AY 17 aqueous solution in a water bath shaker (GFL 1086, Germany) at 150 rpm for 24 h (Fig. 1(d)), they still maintained their physical integrity. On the basis of the experiments and literatures, drying process had little effect on the physical integrity of aerobic granular sludge.

2.2. Dye

AY 17 (C.I. number = 18965, molecular formula = $C_{16}H_{10}Cl_2N_4Na_2O_7S_2$, λ_{max} = 402 nm), was purchased from Tianjin Shengda Chemical Factory (China), and was used without further purification. Its molecular structure is shown in Fig. 2. All the solutions used in the test were obtained by diluting the 200 mg/L of stock AY 17 solution which was prepared by dissolving accurately weighted dye in distilled water.

2.3. Batch biosorption experiments

Batch biosorption experiments were conducted in 250 mL glass stopper Erlenmeyer flasks which were agitated in a water bath shaker with a shaking rate of 150 rpm at a constant temperature of $20 \pm 1\,^{\circ}C$ (but not applicable for isotherms, kinetics and thermodynamics experiments) until reaching equilibrium. Each test lasted for 24 h. The required pH value of the solutions was adjusted with 0.1 mol/L HCl or NaOH solutions with a pH-meter (WTW 340i, Germany) for the measurements. Samples were taken at given time

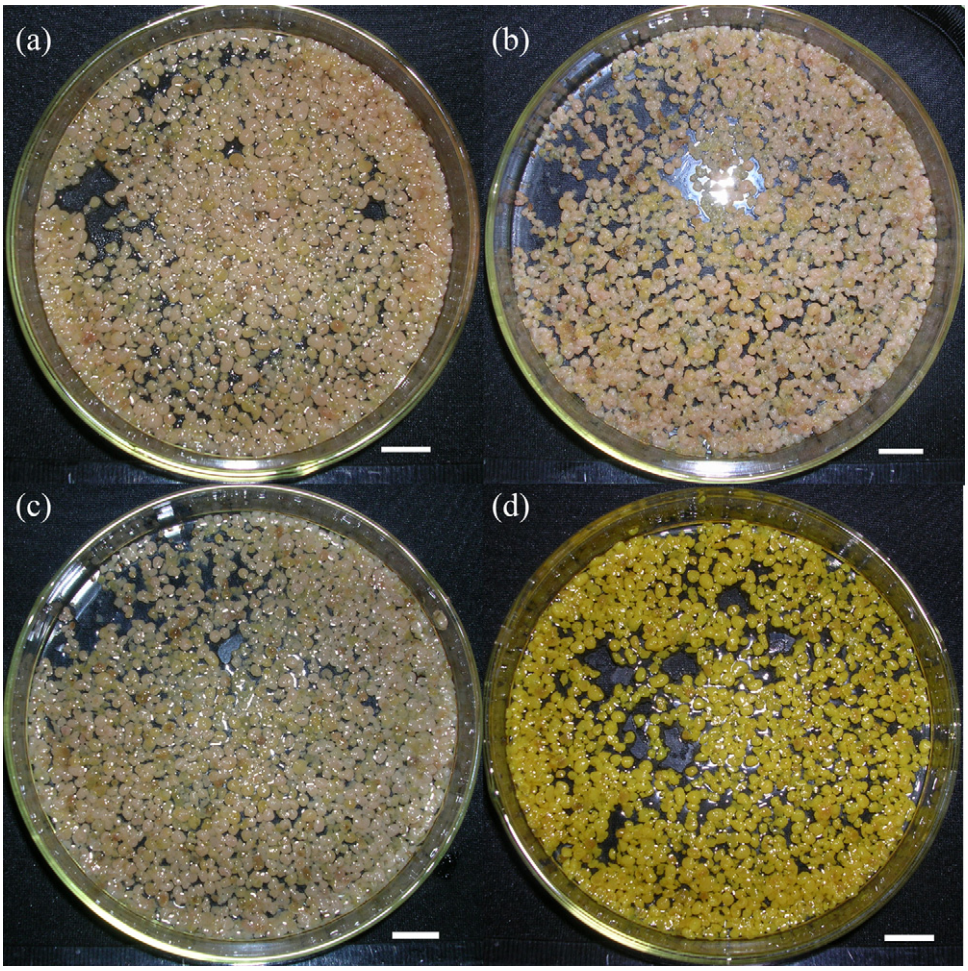

Fig. 1. Images of aerobic granular sludge: (a) living aerobic granular sludge; (b) non-living aerobic granular sludge (dried at 105 °C for 2 h); (c) non-living aerobic granular sludge immersed in distilled water at room temperature for 1 min; (d) non-living aerobic granular sludge after AY 17 biosorption (C_0 = 50 mg/L, temperature = 20 ± 1 °C, biosorbent dosage = 3.0 g/L, initial pH = 2.0 ± 0.1), bar = 10 mm.

intervals and were centrifuged at 3200 rpm for 2 min, and then the supernatant was analyzed for the residual AY 17 concentration by using a UV–vis spectrophotometer (UV-2100, Unico, Shanghai, China).

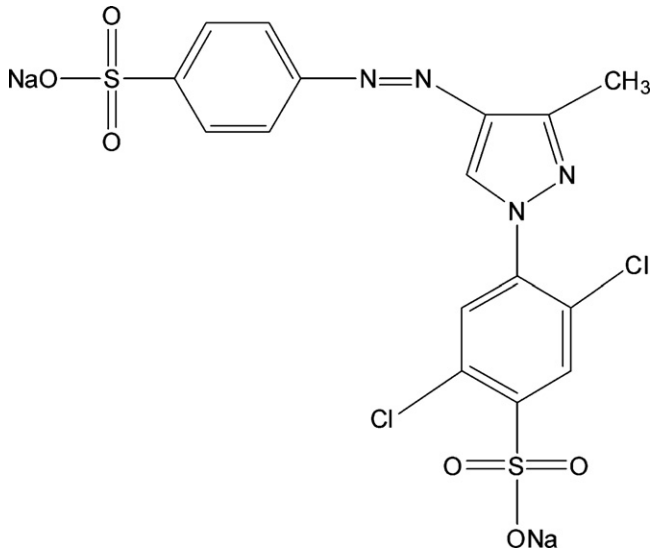

Fig. 2. Chemical structure of AY 17.

In order to investigate the effect of pH value on the biosorption capacity, the initial pH value varied in the range of 1–12, the non-living aerobic granular sludge concentration was fixed at 2.2 g/L, and the initial AY 17 concentration was 40 mg/L. The optimal pH value (2.0 ± 0.1) was used for the subsequent experiments. To study the effect of biosorbent dosage, the amount of the non-living aerobic granular sludge was varying from 0.8 to 4.5 g/L, initial AY 17 concentration was fixed at 65 mg/L. The optimal biosorbent dosage of 3.0 g/L was chosen for the successive experiments. To investigate the effect of initial dye concentration on biosorption, initial AY 17 concentration ranged from 20 to 100 mg/L (20, 40, 60, 80, 100 mg/L). To study the effect of salinity, different concentrations of NaCl (w/v, 0, 0.5, 1, 2 and 3%) were added at an initial AY 17 concentration of 60 mg/L. The equilibrium, kinetics and thermodynamic experiments were performed at temperatures in the range of 20–50 °C, and initial AY 17 concentration was in the range of 20–100 mg/L.

2.4. Analysis

There are two frequently used methods to separate the adsorbents from the aqueous solution for analyzing the liquid portion for the residual, final, equilibrium sorbate concentration, i.e., filtration [8] and centrifugation [12]. Because some dyes could be adsorbed onto the filter papers, filtration was not chosen in the experiments. In the batch biosorption experiments, the samples contained dye

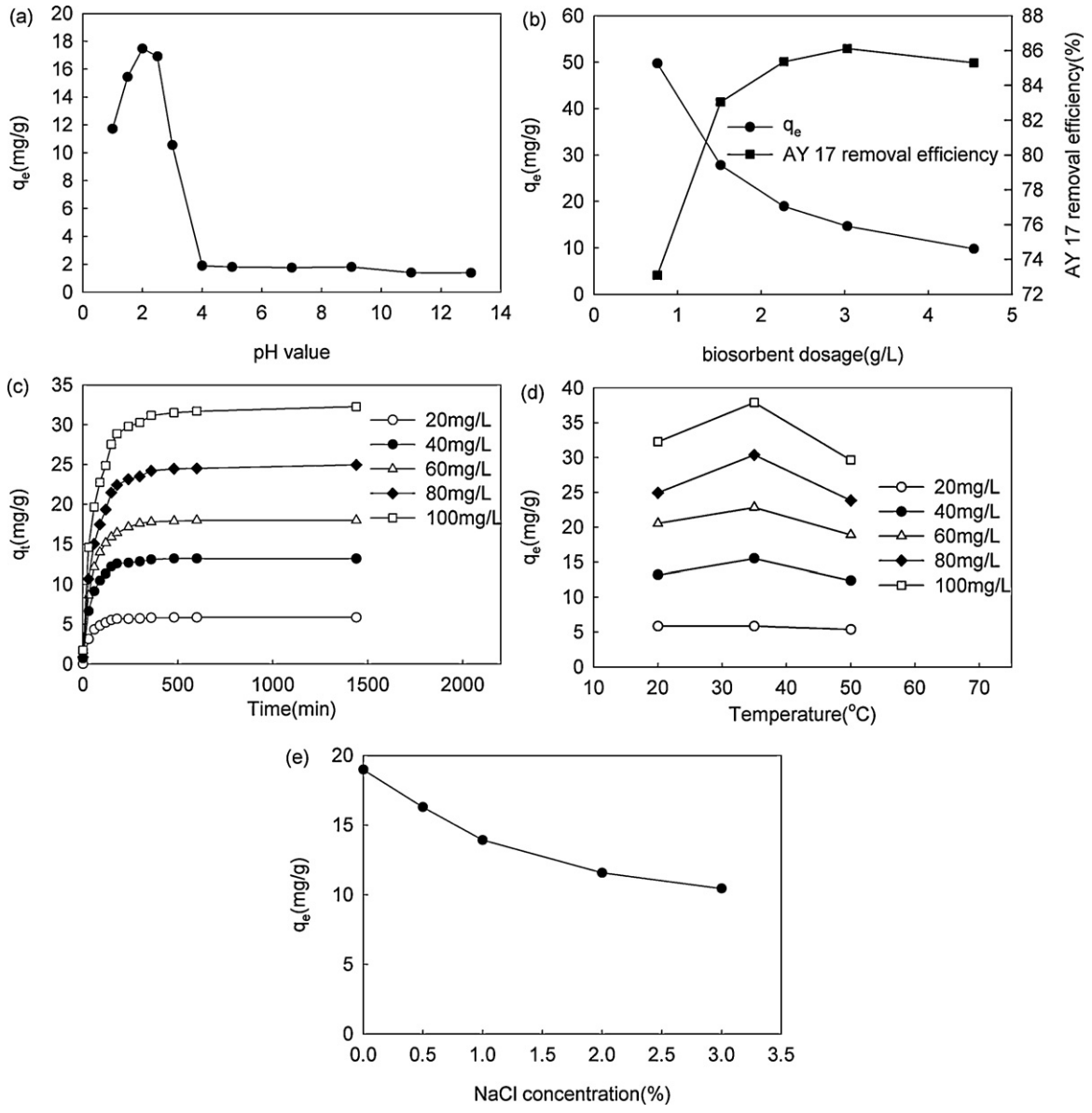

Fig. 3. Effects of (a) pH (C_0 = 40 mg/L, biosorbent dosage = 2.2 g/L, temperature = 20 ± 1 °C); (b) biosorbent dosage (C_0 = 65 mg/L, initial pH = 2.0 ± 0.1, temperature = 20 ± 1 °C); (c) initial dye concentration (biosorbent dosage = 3.0 g/L, initial pH = 2.0 ± 0.1, temperature = 20 ± 1 °C); (d) temperature (biosorbent dosage = 3.0 g/L, initial pH = 2.0 ± 0.1, initial dye concentration: 20–100 mg/L); (e) NaCl concentration (C_0 = 60 mg/L, biosorbent dosage = 3.0 g/L, initial pH = 2.0 ± 0.1, temperature = 20 ± 1 °C) on the biosorption of AY 17 by non-living aerobic granular sludge.

and biosorbent, the biosorption reaction was still ongoing, to guarantee the accuracy and instant of chemical analysis, samples were taken at given time intervals and were centrifuged at 3200 rpm for 2 min, and then the supernatant was analyzed for the residual AY 17 concentration by using a UV–vis spectrophotometer at 402 nm. The dye concentration was calculated from a calibration curve of absorbance versus concentration of the dye solution.

The mean settling velocity of the aerobic granular sludge was 33 m/h (0.55 m/min), and aerobic granular sludge could be completely separated out of the treated effluent by gravity in 1–5 min. In practice, we do not have to use centrifugation, when the biosorption reaction approaches its equilibrium state, 5 min settling is enough, then the treated effluent can be decanted.

Before and after AY 17 biosorption, the non-living aerobic granular sludge was characterized by FTIR using a Bruker Vertex 70 FTIR spectrometer. The aerobic granular sludge was first freeze-dried by using Labconco FreeZone 1L (Labconoco, USA), then they were mixed with KBr in the ratio of 1:100 and compacted to pellet form under high pressure. The pellet was immediately analyzed in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

The amount of AY 17 adsorbed by aerobic granular sludge at equilibrium, q_e (mg/g), was calculated as:

$$q_e = \frac{V(C_0 - C_e)}{M} \quad (1)$$

where C_0 is the initial dye concentration in the solution (mg/L); C_e is the liquid phase dye concentration at equilibrium (mg/L); V is the volume of solution (L); and M is the weight of biosorbent used (g).

3. Results and discussion

3.1. The factors affecting AY 17 biosorption

3.1.1. Effect of initial pH

Fig. 3(a) shows the relationship between the dye biosorption capacity and the pH value at 20 ± 1 °C with 40 mg/L AY 17 and

2.2 g/L non-living aerobic granular sludge. As the pH increased from 1.0 to 2.0, the biosorption capacity obviously increased and reached the maximum value of 17.47 mg/g at pH 2.0. But the biosorption equilibrium capacity decreased as the pH increased from 2 to 3. When the pH further increased (>4.0), the biosorption process was restricted and biosorption capacity was less than 1.80 mg/g. The optimal pH value was 2.0 and it was used for the subsequent experiments. Similar result was reported of the pH effect for the biosorption of Acid Red 14 on soy meal hull [38].

It is important to note that dye molecules have many different and complicated structures, and their adsorption behavior is directly related to the chemical structure, the dimensions of the dye organic chains, the number and positioning of the functional groups of the dyes (e.g., sulfonate groups, azo), solution conditions and process variables (e.g., contact time, initial dye concentration, adsorbents dosage and stirring rate) [6]. As is known, pH can affect the site dissociation of the biomass and the solution dye chemistry [6]. The influence of pH on AY 17 biosorption can be demonstrated on the basis of zero charge point for aerobic granular sludge. As an anionic azo dye, AY 17 will produce anionic ion (SO_3^-) in aqueous solutions. The ionic interactions of the colored dye ions (D–SO_3Na) with the amino groups (R–NH_2) on the non-living aerobic granular sludge may be the possible mechanisms of AY 17 biosorption. The zero charge point of non-living aerobic granular sludge was confirmed to be 2.0. For the presence of H^+, the amino groups of non-living aerobic granular sludge (R–NH_2) were protonated.

$$R\text{–}NH_2 + H^+ \rightleftharpoons R\text{–}NH_3^+ \quad (2)$$

In aqueous solution, AY 17 is dissolved and then the sulfonate groups is dissociated and converted to anionic dye ions.

$$D\text{–}SO_3Na \xrightarrow{H_2O} D\text{–}SO_3^- + Na^+ \quad (3)$$

The biosorption process then proceeds because of the electrostatic attraction between these two counter ions.

$$R\text{–}NH_3^+ + D\text{–}SO_3^- \rightleftharpoons R\text{–}NH_3\cdots O_3S\text{–}D \quad (4)$$

When the pH of the solution is lower than the zero charge point, the AY 17 uptake will be increased for the electrostatic force of attraction. As the pH of the system increases higher than the zero charge point, the negatively charged surface site does not favor the biosorption because of the electrostatic repulsion. Similar mechanism was recognized by acid dye adsorption on chitosan [6].

3.1.2. Effect of biosorbent dosage

Fig. 3(b) shows q_e versus different non-living aerobic granular sludge concentration in the range of 0.8–4.5 g/L, initial AY 17 concentration was fixed at 65 mg/L. Their relation is shown in Fig. 3(b). As seen from Fig. 3(b), the equilibrium biosorption capacity for AY 17 decreased with the non-living aerobic granular sludge dosage increasing. This may be due to the decrease in total adsorption surface area available to AY 17 resulting from overlapping or aggregation of adsorption sites [39]. However, the dye removal efficiency increased and remained almost constant after increasing up to a certain limit. The increased adsorbent surface area and availability of more adsorption sites may be the reasons [39,40]. The optimum biosorbent dosage was found to be 3.0 g/L and was used for the successive experiments.

3.1.3. Effect of initial dye concentration

Fig. 3(c) displays the biosorption profile of AY 17 versus contact time at different initial AY 17 concentrations in the range of 20–100 mg/L. A mass of AY 17 in the solution was adsorbed in the first 30 min for all of the initial concentrations studied and then the removed AY 17 amount gradually decreased until equilibrium. The initial concentration supplies an important driving force to overcome all mass transfer resistances of dyes between the aqueous and solid phase, so a higher initial dye concentration will increase the rate at which adsorbate molecules pass from the bulk solution to the adsorbent surface [3]. The equilibrium biosorption capacity of the non-living aerobic granular sludge increased from 5.86 to 32.26 mg/g with increasing initial AY 17 concentration from 20 to 100 mg/L as a result of the increase in the driving force, a higher initial concentration of dye will enhance the biosorption process. A similar trend was observed for the biosorption of Acid Red 274 by *Enteromorpha prolifera* [4].

3.1.4. Effect of temperature

To investigate the effect of temperature, the biosorption of AY 17 on non-living aerobic granular sludge was studied at three different temperatures, i.e., 20 ± 1, 35 ± 1 and $50 \pm 1\,^{\circ}C$, the initial AY 17 concentration varied in the range of 20–100 mg/L. Fig. 3(d) shows that the equilibrium biosorption capacity increased with increasing temperature up to 35 °C and then decreased under different initial AY 17 concentration. The decrease of the equilibrium uptakes with further increase in temperature means that the dye biosorption process is exothermic and the physical bonding between the dye molecules and the active sites of the non-living aerobic granular sludge will weaken with increasing temperature. Also with the increase of temperature, the solubility of the AY 17 also increases, the interaction forces between the solute and the solvent become stronger than those between solute and biosorbent, consequently the solute is more difficult to adsorb [6].

3.1.5. Effect of salinity

The spent dye bath effluents contain lots of salts. Therefore, it is important to assess the biosorption by non-living aerobic granular sludge at an appropriate salt concentration. Fig. 3(e) shows the results of biosorption tests in the NaCl concentration of 0–3%. As the concentration of NaCl increased from 0 to 1%, the q_e decreased from 18.98 to 10.44 mg/g; however, the ratio of decreasing is visible smaller in the range of 1–3%. According to Eq. (3), at a low NaCl concentration, the common ion effect of Na^+ caused a decreased of D–SO_3^-, and as a result, the dyes biosorption on non-living aerobic granular sludge was reduced. This effect in solution would reduce the electrostatic attraction force between R–NH_3^+ and D–SO_3^- (Eq. (3)). When the NaCl concentration was higher than 1%, the salts enhanced the dissociation of AY 17 molecules and thus favored its precipitation on non-living aerobic granular sludge, suggesting an aggregation mechanism increasing the adsorption capacity in the presence of salts [6].

3.2. Equilibrium isotherm

Isotherm represents the relationship between the adsorption capacity of dyes at constant temperature and the liquid phase dye concentration. In order to design the adsorption system and evaluate the applicability of the sorption process, it is important to establish the most appropriate isotherm model for the equilibrium curve. Three different adsorption isotherms were tested to find the most suitable one: Langmuir, Freundlich and Temkin isotherm models [29–31].

3.2.1. The Langmuir isotherm

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. It is given as

$$q_e = \frac{Q^0 b C_e}{1 + bC_e} \quad (5)$$

where Q^0 and b are Langmuir's constants related to the capacity and energy of the adsorption, respectively. A well-known linear form of

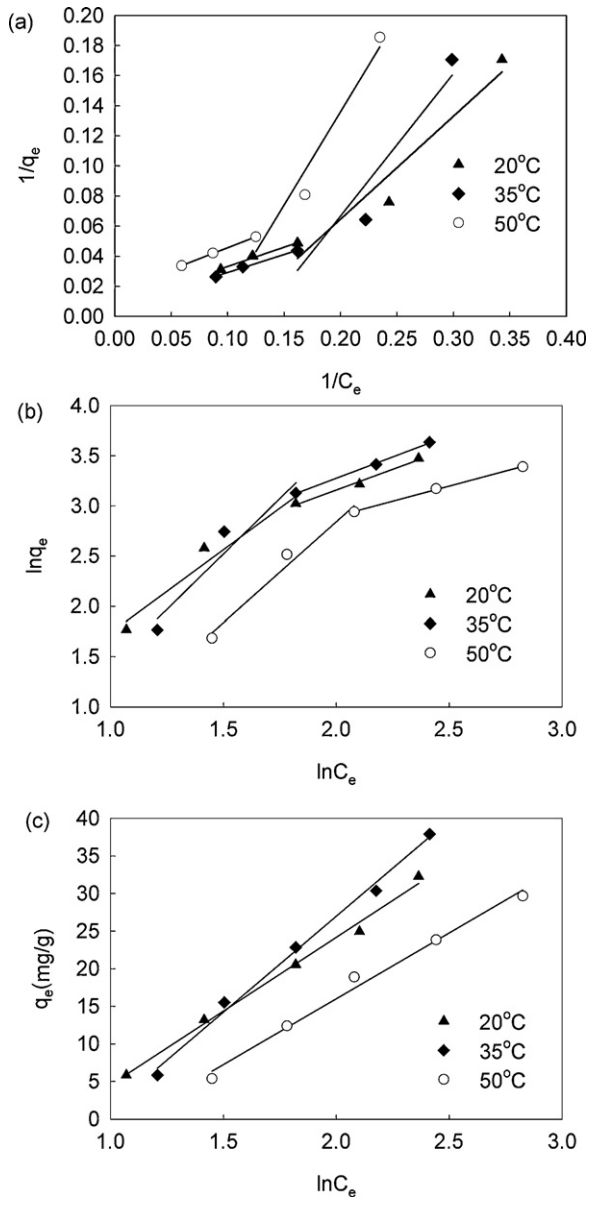

Fig. 4. Biosorption isotherms for AY 17 biosorption by non-living aerobic granular sludge at different temperatures: (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Temkin isotherm (C_0 = 20, 40, 60, 80 and 100 mg/L, biosorbent dosage = 3.0 g/L, initial pH = 2.0 ± 0.1, temperature = 20 ± 1, 35 ± 1 and 50 ± 1 °C).

Langmuir equation is written as

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0C_e} \quad (6)$$

Fig. 4(a) shows the linearized Langmuir isotherm of AY 17 on non-living aerobic granular sludge obtained at 20 ± 1, 35 ± 1 and 50 ± 1 °C. The constants values calculated from the linear forms are given in Table 1. As seen from Fig. 4(a), the Langmuir linear plot deviates from linearity for the whole concentration range. Table 1 shows the Langmuir constants were negative and the values of the correlation coefficients were at the range of 0.8492–0.9167, so Langmuir isotherm was not appropriate for describing the experimental data. However, if the whole concentration range is divided into two regions, i.e., region 1 (20–60 mg/L) and region 2 (60–100 mg/L), excellent fits to the experimental data can be obtained with the Langmuir isotherm at the higher concentration region 2 (Fig. 4(a)). Table 1 also shows the Langmuir isotherm constants, Q^0 and b along with the correlation coefficients for

Table 1
Isotherm constants for the biosorption of AY 17 on non-living aerobic granular sludge at various temperature (C_0 = 20, 40, 60, 80 and 100 mg/L, biosorbent dosage = 3.0 g/L, initial pH = 2.0 ± 0.1, temperature = 20 ± 1, 35 ± 1 and 50 ± 1 °C).

	Temperature (°C)		
	20	35	50
Langmuir, the whole concentration range (20–100 mg/L)			
Q^0 (mg/g)	−32.26	−21.41	−28.99
b (L/mg)	−0.057	−0.072	−0.039
R^2	0.9167	0.8492	0.8792
Langmuir, region 1 (20–60 mg/L)			
Q^0 (mg/g)	−13.83	−8.137	−8.945
b (L/mg)	−0.106	−0.130	−0.090
R^2	0.9386	0.9102	0.9596
Langmuir, region 2 (60–100 mg/L)			
Q^0 (mg/g)	133.3	185.2	60.61
b (L/mg)	0.029	0.023	0.057
R^2	0.9870	0.9974	0.9999
Freundlich, the whole concentration range (20–100 mg/L)			
K_F (mg/g) (L/mg)$^{1/n}$	1.856	1.394	1.288
n	0.800	0.700	0.851
R^2	0.9441	0.9010	0.8910
Freundlich, region 1 (20–60 mg/L)			
K_F (mg/g) (L/mg)$^{1/n}$	1.085	0.453	0.313
n	0.604	0.452	0.500
R^2	0.9542	0.9311	0.9765
Freundlich, region 2 (60–100 mg/L)			
K_F (mg/g) (L/mg)$^{1/n}$	4.488	4.835	5.419
n	1.207	1.176	1.659
R^2	0.9898	0.9982	0.9990
Temkin, the whole concentration range (20–100 mg/L)			
A (L/mg)	0.464	0.389	0.338
B	19.63	25.53	17.49
R^2	0.9936	0.9938	0.9891

the different concentration regions at all temperatures studied. At the lower concentration region 1, Q^0 and b were negative, the experimental data did not fit for Langmuir isotherm. At the higher concentration region 2, Q^0 and b were positive, Q^0 increased with the increasing temperature up to 35 °C, then decrease, indicating that the biosorption process was exothermic in nature; also seen from Table 1, correlation coefficients were close to 1.0 for all the temperatures studied, suggesting that Langmuir isotherm model was applicable for describing the AY 17 biosorption equilibrium on non-living aerobic granular sludge at the higher concentration region 2 (60–100 mg/L).

Reported Q^0 values of other low-cost adsorbents for the adsorption of acid dyes were listed in Table 2. Q^0 in this study was 133.3 mg/g, which was comparable to those of some other adsorbents, clearly indicating that non-living aerobic granular sludge was an efficient and low-cost adsorbent for the removal of acid dyes from wastewater.

3.2.2. The Freundlich isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems, and adsorption capacity is related to the concentration of dye at equilibrium. This isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (7)$$

where K_F and n are the Freundlich constant and the heterogeneity factor, respectively. The linear form of Freundlich isotherm equation is

$$\ln\ q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (8)$$

Table 2
Adsorption capacity for the removal of acid dyes from aqueous solutions by some low-cost adsorbents.

Acid dyes	Adsorbents	Q^0 (mg/g)	Reference
Acid Yellow 17	Non-living aerobic granular sludge	133.3	This study
Acid Yellow 17	Calcined alunite	151.5	[41]
Acid Yellow 36 (metanil yellow)	Waste carbon slurries	211	[11]
Acid Yellow 36	Rice husk carbon	86.9	[42]
Acid Orange 10	Activated carbon prepared from sugarcane bagasse	5.78	[43]
Acid Orange 52 (methyl orange)	Banana peel	21	[44]
Acid Red 14	Soy meal hull	109.89	[38]
Acid Red 57	*Neurospora crassa*	113.6	[45]
Acid Red 114	Activated pongam seed shells	204	[46]
Acid Red 274	*Enteromorpha prolifera*	238.1	[4]

Fig. 4(b) shows the equilibrium data in Freundlich isotherm expressions at 20 ± 1, 35 ± 1, and 50 ± 1 °C. The values of K_F and n obtained from the intercept and the slope of the plot of ln q_e versus ln C_e are also given in Table 1 along with the correlation coefficients.

Fig. 4(b) shows that the Freundlich linear plots deviate from linearity for the whole concentration range. As seen from Table 1, n was lower than unity, indicating that AY 17 was adsorbed unfavorably by non-living aerobic granular sludge at the whole concentration range studied though the correlation coefficients of Freundlich isotherm were close to 1.0.

Whereas, if the whole concentration range is divided into two regions, that is region 1 (20–60 mg/L) and region 2 (60–100 mg/L), good fits to the experimental data can be obtained with the Freundlich isotherm at the higher concentrations (Fig. 4(b)). Table 1 also shows the Freundlich isotherm constants, K_F and n along with the correlation coefficients for the different concentration regions at all temperatures studied. In region 2, the values of n were greater than unity and correlation coefficients were at the range of 0.9898–0.9990, suggesting that AY 17 was adsorbed favorably by non-living aerobic granular sludge at higher concentration region at all temperatures studied. The two linear regions may be due to biosorption occurring at different adsorption sites, e.g., amino, carboxyl, or hydroxyl, owing to different surface groups with different levels of activation energies for the range of sorption reactions [47], as shown later by the FTIR spectra.

3.2.3. The Temkin isotherm

The Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has been used in the following form:

$$q_e = \frac{RT}{b} \ln AC_e \tag{9}$$

The linear form of Temkin isotherm equation is

$$q_e = B \ln A + B \ln C_e \tag{10}$$

where $B = RT/b$, T is the absolute temperature in K, R is the universal gas constant, 8.314 J/mol/K, A is the equilibrium binding constant (L/mg) and B is related to the heat of adsorption. The linear forms of Temkin isotherm plots are presented in Fig. 4(c). The values of the Temkin constants and the correlation coefficient calculated from Fig. 4(c) are listed in Table 1. As seen from Table 1, the Temkin constant B (the heat of adsorption) increased with the increasing temperature up to 35 °C, then decreased, indicating exothermic adsorption.

By comparing the correlation coefficients and other parameters determined by these three isotherms, the correlation coefficients obtained from Temkin isotherm were at the range of 0.9891–0.9938 for the entire concentration range at all the temperatures studied, indicating that the Temkin isotherm yields a much better fit than Freundlich and Langmuir isotherm. Both Freundlich and Langmuir isotherm agreed with the experimental data well at the higher concentration region, indicating the range and distribution of the binding energies should depend strongly on the density and distribution of functional groups both on the dye and adsorbent surfaces [48].

3.3. Biosorption kinetic

Three kinetic models, i.e., pseudo-first-order model, pseudo-second-order model and intraparticle diffusion model, were applied in this study to investigate the reaction pathways and potential rate limiting steps of the biosorption of AY 17 onto non-living aerobic granular sludge.

3.3.1. Pseudo-first-order and pseudo-second-order kinetic model

The pseudo-first-order rate expression of Lagergren model [32] is generally expressed as follows:

$$\log(q_e - q_t) = \log\ q_e - \frac{k_1 t}{2.303} \tag{11}$$

Table 3
Rate constants of pseudo-first-order and pseudo-second-order kinetic models for biosorption of AY 17 by non-living aerobic granular sludge at different initial concentration (C_0 = 20, 40, 60, 80 and 100 mg/L, temperature = 20 ± 1 °C) and different temperatures (C_0 = 60 mg/L, temperature = 20 ± 1, 35 ± 1 and 50 ± 1 °C) (biosorbent dosage = 3.0 g/L, initial pH = 2.0 ± 0.1).

	Pseudo-first-order constants			Pseudo-second-order constants			$q_{e,exp}$ (mg/g)
	k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/(mg min))	$q_{e,cal}$ (mg/g)	R^2	
C_0 (mg/L)							
20	0.021	5.34	0.9970	0.010	5.95	0.9998	5.86
40	0.019	12.33	0.9907	0.004	13.46	0.9997	13.18
60	0.017	16.32	0.9964	0.002	18.38	0.9996	18.00
80	0.015	23.74	0.9872	0.001	25.71	0.9998	24.96
100	0.015	29.84	0.9790	0.001	33.11	0.9997	32.76
T (°C)							
20	0.017	16.32	0.9964	0.002	18.38	0.9996	18.00
35	0.026	21.44	0.9946	0.003	23.15	0.9999	22.85
50	0.034	17.68	0.9915	0.005	19.19	0.9998	18.80

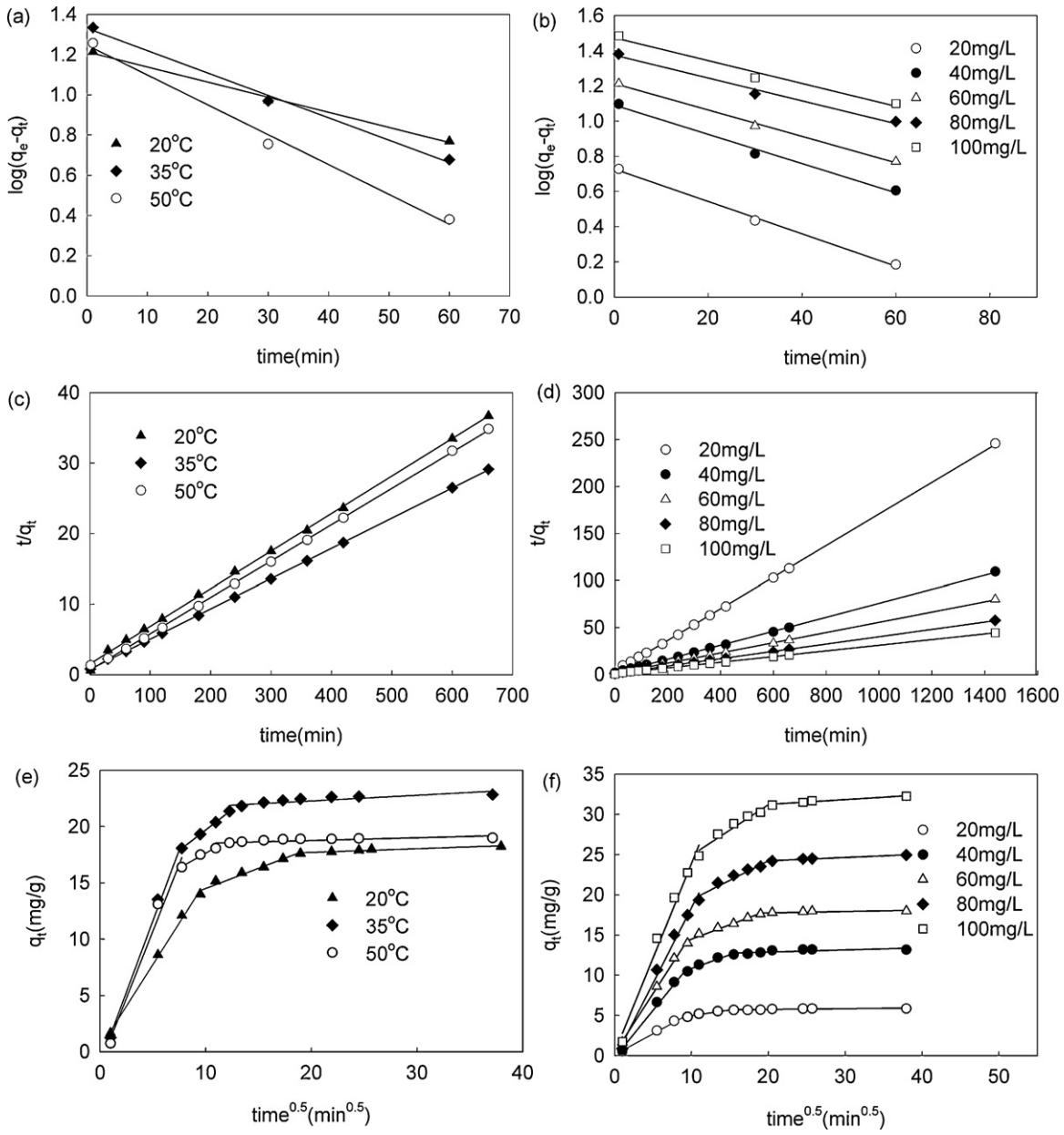

Fig. 5. Kinetic models for biosorption of AY 17 by non-living aerobic granular sludge at different initial concentration (C_0 = 20, 40, 60, 80 and 100 mg/L, temperature = 20 ± 1 °C) and different temperatures (C_0 = 60 mg/L, temperature = 20 ± 1, 35 ± 1 and 50 ± 1 °C): (a) and (b) pseudo-first-order model; (c) and (d) pseudo-second-order model; (e) and (f) intraparticle diffusion model (biosorbent dosage = 3.0 g/L, initial pH = 2.0 ± 0.1).

where q_t and q_e are the dye amounts adsorbed at time t and at equilibrium (mg/g), and k_1 is the pseudo-first-order rate constant for the adsorption process (min^{-1}).

The pseudo-second-order kinetic model of Ho and McKay [33] can be represented in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{12}$$

where k_2 is the pseudo-second-order rate constant (g/(mg min)).

By plotting of $\log(q_e - q_t)$ against t and t/q_t versus t for different temperatures and initial dye concentrations, linear lines were obtained as shown in Fig. 5(a–d). The constants calculated from slope and intercept of plots for the two models are given in Table 3.

For pseudo-first-order plot, correlation coefficients were found to be 0.9790–0.9970, but the calculated values of $q_{e,cal}$ were lower than the experimental $q_{e,exp}$. These results suggest that the model was unsuitable to fit the experimental data for the biosorption of AY 17 onto the non-living aerobic granular sludge. In most cases, it has been reported that the sorption data were well represented by the Lagergren first-order rate equation only in the first 30–50 min of the sorption process [33].

For pseudo-second-order plot, the correlation coefficients were all greater than 0.9996 and even the lowest one in this case was higher than the ones of the pseudo-first-order model. Also the theoretical values of $q_{e,cal}$ agreed well with the experimental data. Further from Table 3, the pseudo-second-order rate constant k_2 decreased with the increasing initial dye concentration. The pseudo-second-order model predicts the biosorption behavior over entire sorption time studied and it is in agreement with the chemisorption mechanism being the rate controlling step [33]. Therefore, the biosorption of AY 17 onto non-living aerobic granular sludge could be well described by the pseudo-second-order model at the entire biosorption time.

Table 4
Rate constants of intraparticle diffusion model for biosorption of AY 17 by non-living aerobic granular sludge at different initial concentration (C_0 = 20, 40, 60, 80 and 100 mg/L, temperature = 20 ± 1 °C) and different temperatures (C_0 = 60 mg/L, temperature = 20 ± 1, 35 ± 1 and 50 ± 1 °C) (biosorbent dosage = 3.0 g/L, initial pH = 2.0 ± 0.1).

	k_{int} (mg/(g min$^{1/2}$))	I (mg/g)	R^2
C_0 (mg/L)			
20	0.210	2.78	0.9640
40	0.345	7.38	0.9580
60	0.357	10.92	0.9726
80	0.479	14.64	0.9516
100	0.626	18.67	0.9549
T (°C)			
20	0.357	10.92	0.9726
35	0.582	13.75	0.9784
50	0.527	12.38	0.9813

3.3.2. Intraparticle diffusion model

If intraparticle diffusion is the rate-limiting factor, biosorption of the adsorbate varies with the square root of time [34]. According to this theory, the intraparticle diffusion model can be expressed as follows:

$$q_t = k_{int} t^{1/2} + I \quad (13)$$

where k_{int} is the intraparticle diffusion rate constant (mg/(g min$^{1/2}$)) and I is the intercept (mg/g).

As shown in Fig. 5(e and f), which shows the plots of q_t versus $t^{1/2}$ for different temperatures and different initial dye concentrations, all the curves had the same features: an initial curve portion followed by a linear portion and then a plateau, indicating that there were different stages occurred in the biosorption process. The initial portion was due to boundary layer diffusion, the linear portion to the intraparticle diffusion, and the plateau to the equilibrium. The values of k_{int} and I obtained from the second linear portion are listed in Table 4. The values of correlation coefficients R^2 were at a range of 0.9516 and 0.9813, suggesting that the intraparticle diffusion model was suitable to fit the experimental data. However, the liner lines did not pass through the origin, expressing that the intraparticle diffusion was present, but not the only rate-limiting step, and boundary layer diffusion might be involved in the biosorption. The k_{int} was higher at a higher initial AY 17 concentration, suggesting the increasing effect of dye concentration gradient. Values of I increased with an increase of initial AY 17 concentration. Further from Fig. 5(e and f), the k_{int} increased as the increasing of I values, supporting that I gives an idea about the thickness of the boundary layer, i.e., the larger the intercept the greater the boundary layer effect. Similar observation was also reported for the biosorption of 2,4-dichlorophenol onto non-living mycelial pellets of *Phanerochaete chrysosporium* [49].

3.4. Thermodynamic analysis

The thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°) and Gibbs free energy change (ΔG°) were determined by the Eq. (14) and Van't Hoff (Eq. (15)).

$$\Delta G^\circ = -RT \ln K_p \quad (14)$$

$$\ln K_p = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

where R is the gas constant, T is temperature in K and K_p is the equilibrium constant (the ratio of the equilibrium concentration of AY 17 on the biosorbent to that in the solution). The values of ΔG° at different temperatures are listed in Table 5. Fig. 6 shows the plot of $\ln K_p$ as a function of $1/T$. The values of ΔH° and ΔS° obtained from the slope and intercept of the plot are also summarized in Table 5.

Table 5
Thermodynamic parameters of AY 17 biosorption by non-living aerobic granular sludge.

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/(mol K))
293	−5.14		
308	−5.13	−9.84	−15.79
323	−4.65		

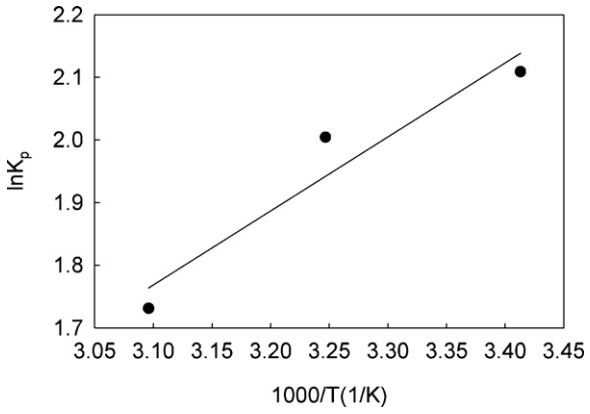

Fig. 6. Van't Hoff plot of biosorption of AY 17 onto non-living aerobic granular sludge.

As seen from Table 5, the values of ΔG° were found to be −5.14, −5.13 and −4.65 kJ/mol at 293, 308 and 323 K, respectively. The values of ΔG° and ΔH° were negative for all the temperatures studied, indicating that the biosorption process was spontaneous and exothermic, which was consistent with the experimental observations. The negative value of ΔS° shows a decreased disorder at the interface between solid and liquid during biosorption. The similar observations were also reported by Wu and Yu [49].

3.5. FTIR analysis

The origin and nature of the biosorbents such as its physical structure, chemical nature, functional groups (e.g., carboxyl, amino, phosphate and sulfonate) may control the biosorption performance [6]. The FTIR spectra of non-living aerobic granular sludge before and after AY 17 biosorption in the range of 4000–400 cm^{-1} were taken to identify the functional groups in the biosorption. As shown in Fig. 7, the FTIR spectra before and after AY 17 biosorption show significant similarities in the spectra, which can be identified based on the reports in previous studies [23]. The strong band at 3435 cm^{-1} reflected N—H and O—H stretching vibrations

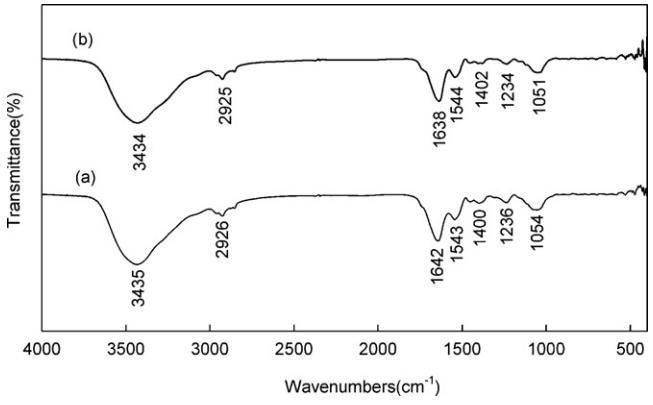

Fig. 7. FTIR spectra of non-living aerobic granular sludge: (a) before AY 17 biosorption; (b) after AY 17 biosorption.

of hydroxyl and amine groups on the surface of the non-living granular sludge, and the band at 2926 cm^{-1} would be due to an asymmetric vibration of CH_2. The band at 1400 cm^{-1} could be assigned to the symmetrical stretching vibration of C=O of carboxylate and deformation vibration of O—H of alcohols. A distinct band at 1642 cm^{-1} was the result of the stretching vibration of C—O and C—N (Amide I) peptidic bond of protein. While a 1543 cm^{-1} band could be due to a combination of the stretching vibration of C—N and deformation vibration of N—H (Amide II) peptidic bond of protein. The band at 1236 cm^{-1} implied the C—N stretching of Amide III [50]. Band at 1054 cm^{-1} could be attributed to the stretching vibration of OH of polysaccharides.

The band intensity at 1642 (Amide I), 1543 (Amide II) and 1236 cm^{-1} (Amide III) all clearly decreased after the AY 17 biosorption, indicating that there would be an interaction of AY 17 with the amine groups from protein, also the band at 1642, 1543 and 1236 cm^{-1} shifted to 1638, 1544 and 1234 cm^{-1}, respectively. After the non-living aerobic granular sludge was loaded with AY 17, the band intensity at 3435, 2926, 1400 and 1054 cm^{-1} all decreased, suggesting that N—H and O—H of hydroxyl and amine, the CH_2 group of lipids, the C=O of carboxylate, OH of polysaccharides were involved in the AY 17 biosorption. And the band at 3435, 2926, 1400 and 1054 cm^{-1} shifted to 3434, 2925, 1402 and 1051 cm^{-1}, respectively.

As for the non-living aerobic granular sludge, it contains mainly bacteria, protozoa and EPS. The cell wall of bacteria, outer membranes of protozoa' eucaryotic cells and EPS compose of mainly protein, lipid, polysaccharides and nucleic acids. Carboxylic acid (—COOH), aldehyde (—COH), hydroxyl (—CHOH), sulfhydryl (—SH), phosphoryl ($—PO_4H_3$) and amine ($—NH_2$) organic compounds are the functional groups in non-living aerobic granular sludge which enable them to bind dyes from the liquid phase [28]. Therefore, the FTIR results show the main chemical functional groups for biosorption of AY 17 onto non-living aerobic granular sludge would be amine, hydroxyl, carboxyl and either.

4. Conclusion

The biosorption of AY 17 from aqueous solution onto non-living aerobic granular sludge has been studied. This biosorption process was highly dependent on the acidic pH and the favorable pH value was 2.0. The biosorption capacity increased with an increase of initial dye concentration, but decreased with increasing biosorbent dosage and NaCl concentration. Temkin isotherm was able to adequately describe this biosorption equilibrium for the whole concentration range. Both Freundlich and Langmuir isotherm agreed well with the experimental data at higher initial dye concentration. The pseudo-second-order model expresses the biosorption kinetics well. Intraparticle diffusion model studies indicate that both boundary layer and pore diffusion might affect the biosorption rate. The analysis by FTIR further revealed that functional groups (e.g., amine, hydroxyl, carboxyl) on aerobic granular sludge would be the active binding sites for the biosorption of the studied dye. Thermodynamic studies demonstrated that the biosorption process was spontaneous and exothermic for the negative value of ΔG° and ΔH°. Due to the excellent settling ability, the aerobic granular sludge can be rapidly and completely separated out of the treated wastewater by gravity, which provides a simple process application compared with bacterial biomass powder. The present work shows that non-living aerobic granular sludge can be effectively used as a low-cost biosorbent for the removal of AY 17 dye from wastewater.

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