Desalination and Water Treatment
www.deswater.com
doi:10.5004/dwt.2017.20827

79 (2017) 329–337
June

Influence, equilibrium, thermodynamic and kinetic investigations on adsorption of 17beta-estradiol by anaerobic granule sludge

Bai-Hang Zhao*, Jie-Yi Zhai, Jie Chen, Wei Bian, Jun Li*

Department of Municipal Engineering, Beijing University of Technology, Beijing, 100124, China,
email: bhzh@bjut.edu.cn (B.H. Zhao), ZJY20141105@emails.bjut.edu.cn (J.Y. Zhai), 201504052@emails.bjut.edu.cn (J. Chen), yangzhoubw@126.com (W. Bian), jglijun@bjut.edu.cn (J. Li)

Received 25 October 2016; Accepted 13 April 2017

ABSTRACT

The effects of adsorbate concentration, adsorbent concentration, temperature, pH, and ion strength on the 17beta-estradiol (E2) adsorption process by anaerobic granular sludge (AnGS) were investigated in this study. The adsorption process was analyzed according to adsorption isotherm, adsorption thermodynamics and adsorption kinetics. It was found that E2 was quickly and effectively adsorbed by AnGS. The adsorption capacity and adsorption removal efficiency of E2 increased as E2 concentration increased, and decreased as AnGS concentration increased. Low temperature, low pH, and low ionic strength promoted E2 adsorption by AnGS. The Freundlich absorption isotherm accurately described the E2 adsorption equilibrium process by AnGS and the pseudo-second-order model accurately described the adsorption kinetics. The overall adsorption process of E2 by AnGS was a physical adsorption process of spontaneous heat release controlled both by film diffusion and intraparticle diffusion.

Keywords: 17beta-estradiol; Anaerobic granular sludge; Adsorption; Thermodynamics; Dynamics

1. Introduction

Estrogens generally exist in rivers, lakes, and other water bodies, resulting in an amorphosis of fish, frogs, and other aquatic animals at low levels (ng/L) [1]. Estrogens in above aquatic system are mainly from WWTPs effluents [2]. It is difficult to prevent estrogens from infiltrating into drinking water. Estrogens are not detected only in water bodies, but also estrogen activities are often strengthened in the chlorine disinfection process of drinking water [3]. In essence, the ingesting of drinking water carries a certain level of risk [4].

The main methods for estrogen removal are physical adsorption, chemical oxidation, and biological degradation [5]. A great deal of attention has been given to biological methods due to the effectiveness and low cost of biological treatment [6–8]. Most research about E2 biological removal has focused on its removal in activated sludge treatment systems [9–11], owing to estrogen flow into WWTPs with domestic wastewater. Adsorbed estrogens in activated sludge enter into strictly anaerobic environments and potentially are released into surrounding water following the process of sludge anaerobic digestion [12]. Hence, estrogen removal under anaerobic conditions is important for ultimately removing and preventing estrogens to flow into aquatic system.

Estrogen transformation in strictly anaerobic environment has been reported by many researches [13–15]. Monsalvo et al. [15] investigated the biological removal efficiency of five estrogens in an anaerobic membrane bioreactor, including 17β-estradiol (60.2%), 17α-estradiol (26.5%), 17α-ethynylestradiol (15.0%), estriol (<1.0%), and estrone (<1.0%). Although Mes et al. [16] thought that it was hard to degrade estrogens in an anaerobic condition. Carballa et al. [17] found that estrogens were removed during the process of sludge anaerobic digestion, and natural estrogens had higher removal efficiency than artificial estrogens. The reported literatures mainly explore estrogen anaerobic transformation during the process of sludge anaerobic digestion. Little information can be found about estrogen removal by anaerobic granular sludge (AnGS).

---

*Corresponding author.

As we all know, adsorption is the first step for the biological removal of organic pollutants. Biodegradation often happens after the adsorption of organic pollutants by biological aggregates. Adsorption plays an important role about estrogen removal in activated sludge treatment system [18,19]. The removal of E2 is a result of biodegradation rather than adsorption by the presence of nitrate in an anaerobic reactor, but adsorption is the predominant process when nitrate is absent in an anaerobic reactor [20]. The adsorption process is also crucial to estrogen removal in anaerobic systems.

Strong adsorption removal of organic pollutants by AnGS has been extensively investigated owing to the advantages of granular sludge's high biomass, high extracellular polymer, and large surface area [21]. Sun et al. [22] investigated acidic dye adsorption removal by AnGS grafted with polyethylenimine, and observed the maximum color removal at low pH value (pH 2.0). Shi et al. [23] explored the competitive adsorption of methylene blue and Pb(II) by AnGS through fourier transform infrared spectroscopy and fluorescence spectroscopy. The adsorption removal of organic pollutants by AnGS has been mainly focused on dye. Little information about estrogen adsorption removal by AnGS can be found.

17beta-estradiol (E2) is a typical environmental hormone with high estrogen activity [5,24]. Hence, it was chose to investigate estrogen adsorption process by AnGS. In this study, five influence factors on E2 adsorption by AnGS were investigated. The adsorption equilibrium, adsorption kinetics and adsorption thermodynamics were analyzed.

2. Materials and methods

2.1. Sorbents-sludge, adsorbate, and reagent

AnGS was used as sorbents-sludge and taken from a UASB reactor treating beer wastewater in Yanjing brewery. The sludge was washed with pure water and centrifuged at 3600 rpm for 15 min to remove water-soluble constituents. The specific gravity, sludge settling velocity, and particle size of the AnGS were 1.011–1.023 $g\cdot cm^{-3}$, 13.39 $m\cdot h^{-1}$, and 1–2 mm, respectively. The AnGS was inactivated before the experiment to eliminate estrogen removal through biodegradation. First, the AnGS was stored at –40°C for 10 h to keep the integrity of the particles, and then it was heated to 121°C for 30 min in an autoclave to ensure the loss of biological activity.

E2 was used as adsorbate in the experiment. 17beta-estradiol-2,4,16,16-d4 (E2-d4) was used as an internal standard substance in the analysis process of E2 by GC-MS. The E2, E2-d4, and Bstfa (1%TMCS) were of an analytical reagent grade purchased from Sigma, Germany. Other organic solvents including methanol and ethyl acetate were of chromatographic reagent grade from Sinopharm, China. High purity water was produced using a MilliQ Plus system (Millipore, USA).

2.2. Adsorption experiment

Adsorption studies were conducted by setting a series of batch experiments. The effects of initial E2 concentration, AnGS concentration, temperature, pH, and ionic strength on E2 adsorption by AnGS were investigated. The adsorption tests were carried out in 250 ml serum bottles with 200 mL working volume. After adding E2 and inactivated AnGS into the serum bottles, the bottles were blown for 5 min with high purity nitrogen (99.999%) to remove dissolved oxygen and maintain strictly anaerobic environment. The serum bottles were then quickly sealed with rubber plugs and shaken in a constant temperature oscillator at 120 rpm (Jintan Medical Instrument Factory, BS-1E, China) for 2 h to ensure adsorption equilibrium was reached. The initial pH was adjusted by adding 2 N NaOH or 2 N HCl.

Adsorption capacity (q_e) and adsorption removal efficiency (φ) were used here to evaluate E2 adsorption by AnGS. q_e and φ were calculated as follows:

$$q_e = \frac{\left(C_0 - C_e\right)\cdot V}{X_{VSS}} \tag{1}$$

$$\varphi = \frac{C_0 - C_e}{C_0}\cdot 100\% \tag{2}$$

where q_e ($\mu g\cdot gVSS^{-1}$) is the amount of adsorbed E2 per gram of AnGS when adsorption equilibrium is reached; C_0 ($\mu g\cdot L^{-1}$) is the initial E2 concentration; C_e ($\mu g\cdot L^{-1}$) is the final E2 concentration in liquid phase in each serum bottle; V (L) is the working volume; X_{VSS} (g) is the amount of AnGS used in the experiment; and φ (%) is the adsorption removal efficiency of E2 by AnGS.

Ionic strength (l), the degree of ionic electrical properties in the solution, was expressed as follows:

$$I = \frac{1}{2}\Sigma C_i \cdot Z_i^2 \tag{3}$$

where C_i ($mol\cdot L^{-1}$) is the mass concentration of ion i; Z_i is the valence of ion i.

2.3. Adsorption isotherm models

The adsorption phase equilibrium explains the maximum adsorption capacity of the adsorbent for the adsorbate molecule and the adsorption selectivity. The adsorption isotherm is an important parameter to design and optimize an adsorption system. The adsorption equilibrium data were evaluated by Langmuir, Freundlich, and Tempkin isotherms to describe the interaction of E2 and AnGS when equilibrium was reached between the liquid and solid phases.

The Langmuir isotherm equation is:

$$q_e = \frac{q_{\max}\cdot b\cdot C_e}{1 + b\cdot C_e} \tag{4}$$

where $q_{\max}$ ($\mu g\cdot gVSS^{-1}$) is the maximum adsorption capacity of AnGS; b ($L\cdot \mu g^{-1}$) is the adsorption equilibrium constant.

The Freundlich isotherm equation is:

$$q_e = K_f \cdot C_e^{1/n} \tag{5}$$

where K_f ($L\cdot gVSS^{-1}$) is a constant related to the AnGS adsorption capacity and n is an empirical parameter related to adsorption intensity, which changes with the adsorbent's heterogeneity.

The Tempkin isotherm equation is:

$$q_e = B\cdot\ln C_e + B\cdot\ln A \tag{6}$$

where B is a dimensionless constant related to the temperature and adsorption properties of the adsorbent; A is the equilibrium constant of the maximum binding energy (L·g^{-1}).

2.4. Adsorption thermodynamic

To further study the effect of temperature on E2 adsorption by AnGS, the thermodynamic behavior was investigated and analyzed by Gibbs equation. The Gibbs free energy exchange (ΔG°), adsorption entropy exchange (ΔS°), and adsorption enthalpy exchange (ΔH°) in the adsorption process were calculated using the following equations:

$$K_d = \frac{q_e}{C_e} \tag{7}$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R\cdot T} \tag{8}$$

$$\Delta G^0 = \Delta H^0 - T\cdot\Delta S^0 \tag{9}$$

where K_d is the distribution coefficient of E2 in the solid and liquid phase at equilibrium; R (kJ·mol^{-1}·K^{-1}) is the ideal gas constant (8.314 × 10^{-3}); T (K) is absolute temperature; ΔG° (kJ·mol^{-1}) is the Gibbs free energy; ΔS° (kJ·mol^{-1}·K^{-1}) is the standard entropy change; and ΔH° (kJ·mol^{-1}) is the standard enthalpy change.

2.5. Kinetic adsorption

Adsorption is a time-dependent process. The adsorption rate of a pollutant is an important parameter to evaluate the feasibility of the adsorbent for use in wastewater treatment. To evaluate the adsorption rate and adsorption dynamics mechanism of E2 adsorption by AnGS, three kinetic models were used to describe the adsorption data in our experiment.

The pseudo-first-order kinetic model is:

$$\lg\left(q_e - q_t\right) = \lg q_t - \frac{k_1.t}{2.303} \tag{10}$$

The pseudo-second-order kinetic model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

The intraparticle diffusion model is:

$$q_t = k_3 t^{1/2} + C \tag{12}$$

where q_t (μg·g^{-1}) is the amount of E2 adsorbed at time t; k_1 (min^{-1}) is the adsorption rate constant of the pseudo-first-order model; k_2 (g·μg^{-1}·min^{-1}) is the adsorption rate constant of the pseudo-second-order model; k_3 (g·μg^{-1}·min^{-1}) is the rate constant of internal particle diffusion; $t^{1/2}$ is the half equilibrium time of adsorption process; and C is the thickness of the adsorption boundary layer.

2.6. Analysis

E2 was measured by gas chromatography-mass spectrometry (GC-MC) (Agilent 6890N-5973, UAS). The reaction solution was filtered through a 0.45 um glass fiber membrane (Jinteng, China). The pH of the filtered water sample was adjusted to 2.0–3.0 by 10% HCl. Solid phase extraction (SPE) was used to extract E2 in the filtered samples. The SPE column was activated in turn by 5 mL ethyl acetate, 5 mL methanol, and 10 mL ultra-pure water before use. The E2 in the filtered water sample was enriched in the activated SPE column with a flow rate of 5 mL·min^{-1}. The SPE column was eluted by 10 mL methanol, and 10 mL ethyl acetate was used to extract E2 enriched in the SPE column. The extraction solution was collected in a bottle with 2 mL volume and inundated slowly with nitrogen at 45°C. The E2 in the bottle was treated with 100 μL Bstfa (1% TMCS) for 30 min and then with 50 μL pyridine at 70°C. The derived sample was measured by gas chromatography-mass spectrometry (GC-MC) (Agilent 6890N-5973, UAS) after cooling to room temperature. The sample injection volume was 10 μL.

The gas chromatograph was conducted using an Agilent DB-FFAP(122-3232) (0.25 mm × 30 mm, film thickness 0.25 μm) with Helium as a carrier gas at a flow rate 1.0 mL·min^{-1}. The inlet temperature was set to 250°C, and the initial temperature of ramping oven was set to 100°C for 1 min. The temperature of the ramping oven was raised to 200°C at a rate of 10°C·min^{-1}, then to 300°C at a rate of 3°C·min^{-1}. The mass spectrometer conditions were ionization mode, EI, with electron energy at 70 eV, interface temperature of 280°C, ion source temperature of 230°C, quadropole temperature of 150°C, and a solvent delay of 15 min.

3. Results and discussion

3.1. Adsorption characteristics of E2 by AnGS

E2 concentration and E2 removal efficiency were shown in Fig. 1 at initial E2 concentration 10 μg·L^{-1}, AnGS concentration 1.517 gVSS·L^{-1}, pH 7, and temperature 25°C. E2 concentration rapidly decreased to 4.46 μg·L^{-1} after the first

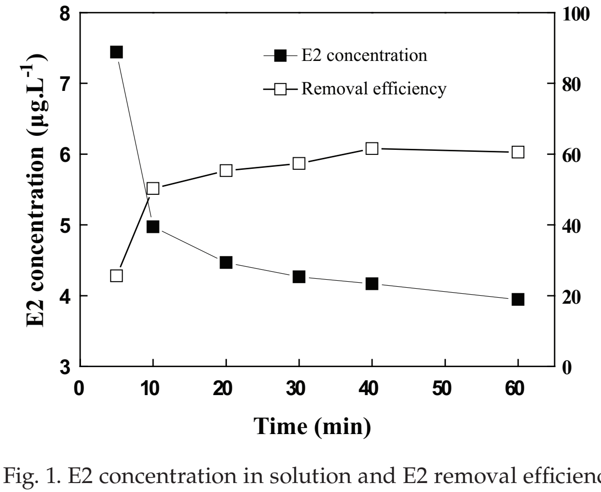

Fig. 1. E2 concentration in solution and E2 removal efficiency at different time.

20 min and then gradually became stable. E2 removal efficiency quickly increased in the first 20 min, reaching about 60.54%. The comparable removal efficiency indicated that E2 could be removed by AnGS adsorption.

3.2. Effect of operating factors on E2 adsorption

3.2.1. Effect of initial E2 concentration

Effect of initial E2 concentration on E2 adsorption by AnGS was investigated at AnGS concentration 1.517 gVSS·L^{-1}, pH 7, and temperature 25°C. Adsorption capacity was used to represent AnGS adsorption ability for E2. The experimental data were shown in Fig. 2. The AnGS adsorption capacity increased with time under different initial E2 concentration (2 µg·L^{-1}, 4 µg·L^{-1}, 6 µg·L^{-1}, 8 µg·L^{-1}, 10 µg·L^{-1}, 12 µg·L^{-1}). The AnGS adsorption capacity tended to be stable after about 20 min. Then, the adsorption equilibrium was reached. The saturated adsorption capacity of AnGS for E2 rose from 0.90 µg·g^{-1} to 4.86 µg·g^{-1} as the initial E2 concentration increased from 2 µg·L^{-1} to 12 µg·L^{-1}. The higher substrate concentration in the liquid resulted in more adsorption by adsorbent [25]. The AnGS adsorption capacity for E2 increased with initial E2 concentration ranging from 2 µg·L^{-1} to12 µg·L^{-1}.

The AnGS adsorption capacity for E2 increased at a fast rate in the first 20 min in the experiments with different initial E2 concentration, and then increased at a lower rate until adsorption equilibrium was achieved. The amount of E2 removal in the first 20 min was about 91.37% of the total E2 removal. This illustrated that E2 adsorption removal by AnGS was a fast adsorption process. Similar result is reported by Chiavola et al. [18] who observe a very rapid removal of endocrine disrupting chemicals in the first 30 min by aerobic granular sludge.

A fast adsorption rate was found in the initial adsorption process with high E2 liquid concentration. High E2 concentration can overcome the mass transfer resistance between the liquid and solid, and was beneficial for helping E2 transfer rapidly to AnGS surface. The concentration gradient of E2 between liquid and solid gradually decreased alongside the further adsorption of E2 by AnGS. Then, the migration rate of E2 from liquid to AnGS slowed down, and dynamic balance was achieved when the migration rate of E2 moving to AnGS surface was equal to the rate of E2 moving out from AnGS surface.

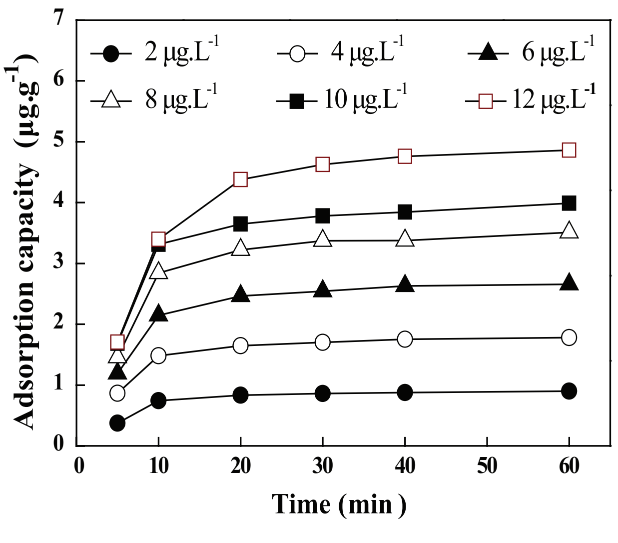

Fig. 2. Effect of initial E2 concentration on E2 adsorption by AnGS.

3.2.2. Effect of AnGS concentration

Effect of AnGS concentration on E2 adsorption by AnGS was investigated at initial E2 concentration 10 µg·L^{-1}, pH 7, and temperature 25°C. The adsorption capacity decreased as AnGS concentration increased from 0.773 gVSS·L^{-1} to 4.59 gVSS·L^{-1} (Fig. 3). The E2 removal efficiency increased from 38.0% to 76.4% as AnGS concentration increased from 0.773 gVSS·L^{-1} to 3.12 gVSS·L^{-1} (Fig. 3). After then, E2 removal efficiency dropped from 76.4% to 74.8% with the raise of AnGS concentration from 3.12 gVSS·L^{-1} to 4.59 gVSS·L^{-1}. More AnGS provided more binding sites for E2 adsorption, which resulted in the increase of E2 removal efficiency. However, after a certain point, the increase of AnGS concentration caused a decrease of E2 removal efficiency. This may be due to the superposition of adsorption sites or blockage caused by high adsorbent concentration [26]. Theoretically, an increase of AnGS should have provided a broader surface for E2 adsorption removal, but in fact, the high concentration of adsorbent resulted in a shielding effect which prevented the binding of adsorbents and adsorption sites and decreased the adsorption capacity [27]. It exposed that the adsorption sites of the adsorbent cannot be utilized effectively at high adsorbent concentration, and AnGS adsorption capacity for E2 decreased as AnGS concentration increased.

3.2.3. Effect of temperature

Effect of temperature on E2 adsorption by AnGS was investigated at initial E2 concentration 10 µg·L^{-1}, AnGS concentration 1.517 gVSS·L^{-1}, and pH 7. The experimental data are shown in Fig. 4. As temperature increased from 20°C to 40°C, AnGS adsorption capacity decreased from 4.55 µg·g^{-1}

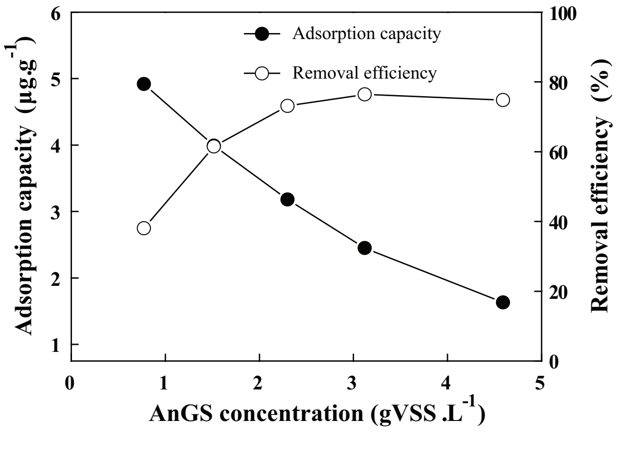

Fig. 3. Effect of AnGS concentration on E2 adsorption by AnGS.

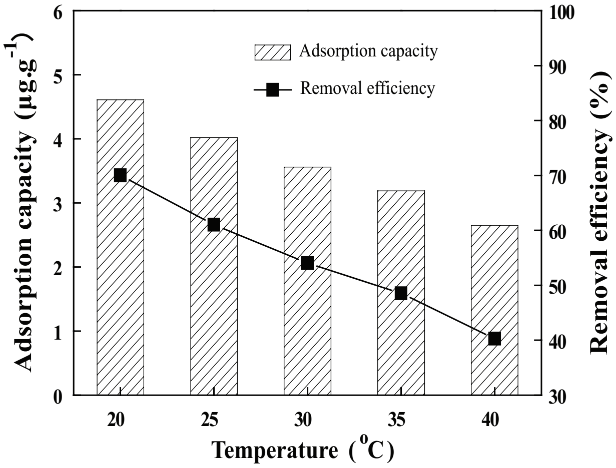

Fig. 4. Effect of temperature on E2 adsorption by AnGS.

to 2.87 μg·g^{-1} and E2 removal efficiency decreased from 70.0% to 40.3%. High temperature was not beneficial to E2 adsorption by AnGS. This may be due to the loss of binding sites at higher temperature [28]. A similar phenomenon has been reported by other researchers [19,29,30]. While Yang et al. [31] found that the adsorption capacity increased as temperature increased during estrogen adsorption in an artificial wetland system.

3.2.4. Effect of pH

The pH of solution has been identified as one of the most important parameters in wastewater treatment process. Effect of pH on AnGS adsorption capacity for E2 was investigated at initial E2 concentration 10 μg·L^{-1}, AnGS concentration 1.517 gVSS·L^{-1}, and temperature 25°C. The pH range in our experiment was set between 5.0 and 10.0, according to common pH values in practical biochemical treatment process. The experimental data were shown in Fig. 5. When pH rose from 5.0 to 10.0, the adsorption capacity decreased from 4.53 μg·g^{-1} to 3.31 μg·g^{-1} and E2 removal efficiency decreased from 68.79% to 50.22%. In other words, a lower pH resulted in a high E2 adsorption capacity and a high E2 removal efficiency in E2 adsorption removal by AnGS.

The set pH influences the adsorption process in two ways: First, by changing the net charge of adsorbate and absorbent [32] , and second, by affecting adsorbate solubility [33]. E2 has a functional group of hydroxyl and unsaturated bonds, which may result in a pH-dependent net change for E2 molecules [34]. And, the surface of AnGS also has a net negative charge. At lower pH values, E2 combined with H$^+$ and produced a net positive charge which promoted the combination of E2 and AnGS. Because of this, lower pH promoted the AnGS adsorption capacity for E2 and increased E2 removal efficiency. The amount of negative charged in the solution increased at high pH values (pH > 7), discouraging E2 and AnGS combination due to the repulsion of like charges. In addition, E2 solubility increased to 10.46 ± 0.03 as pH increased from 7 to 12 [35]. This high solubility caused the ionization and dissolution of E2 at high pH, which resulted in the release of adsorbed mass to the liquid phase.

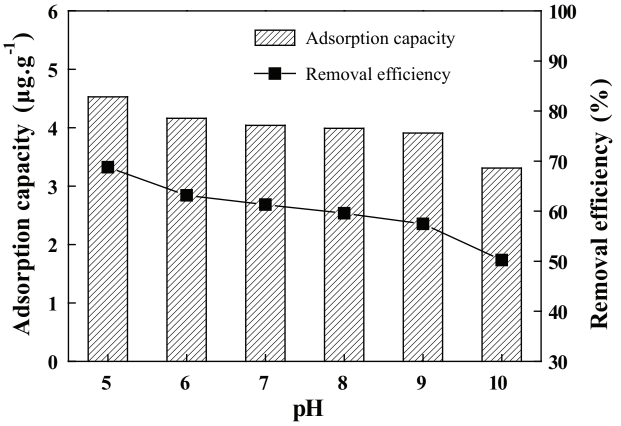

Fig. 5. Effect of pH on E2 adsorption by AnGS.

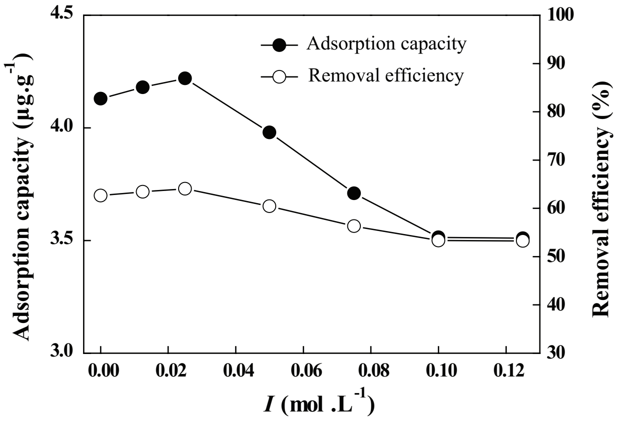

Fig. 6. Effect of ionic strength (NaCl) on E2 adsorption by AnGS.

3.2.5. Effect of ionic strength (NaCl)

Ions are normal compositions in wastewater treatment reactors [19, 29]. NaCl was selected to investigate the effect of ionic strength on E2 adsorption removal by AnGS by virtue of its ubiquity. The experiment was conducted at E2 concentration 10 μg·L^{-1}, AnGS concentration 1.517 gVSS·L^{-1}, pH 7 and temperature 25°C. The experimental data were shown in Fig. 6. With the increasing of ionic strength, the AnGS adsorption capacity for E2 at first slowly increased and then rapidly decreased until it became stable. A similar phenomenon was observed concerning E2 adsorption removal efficiency (Fig. 6). NaCl played a promoted role in the adsorption process at lower ionic strength.

When ionic strength increased from 0 mol·L^{-1} to 0.025 mol·L^{-1}, the double electric layer between the surface of the adsorbate and adsorbent began to be compressed and the effective adsorption sites in the adsorbent surface were reduced. The distance between AnGS and E2 would be shortened in order to maintain the density and the amount of points, which resulted in enhanced adsorption capacity and E2 removal efficiency [19]. However, the adsorption sites may be mainly grabbed off by ionics with the further increasing of ionic strength [36]. A competitive relationship was exited between ionics and E2 at the adsorption process.

The reduction of available adsorption sites caused by high ionic strength led to the decreasing of AnGS adsorption capacity and E2 removal efficiency.

3.3. Adsorption isotherm

Freundlich, Langmuir and Tempkin isotherms (Eqs. (4)–(6)) were used to describe the adsorption experimental data at initial E2 concentration 10 μg·L^{-1}, AnGS concentration 1.517 gVSS·L^{-1}, pH 7.0 and temperature 25°C (Fig. 7). The coefficients of various isotherms were summarized in Table 1. The correlation coefficients (R^2) of the three isotherms were 0.994, 0.992, and 0.929, respectively. The R^2 values of Freundlich and Langmuir isotherms were higher than that of Tempkin isotherm. The higher R^2 values indicate that Freundlich and Langmuir isotherms more accurately described the experimental data than Tempkin isotherm.

Langmuir isotherm is an idealized model and assumes the surface of the adsorbent is monolayer, uniform, and that the adsorption capacity of all adsorption sites is the same [37]. However, the actual surface of AnGS adsorbent was far from uniform. The adsorption capacities of different AnGS sites were never the same, which was not consistent with the assumptions of Langmuir model. Freundlich isotherm is obtained under the assumption that a heterogeneous source surface has a non-uniformly distributed heat adsorption [38]. Because of this, the Freundlich isotherm was suitable for describing the E2 adsorption process by AnGS.

As a constant, K_f relates to adsorption capacity. A higher K_f value means a higher AnGS adsorption capacity for E2. The value of K_f was determined to be 1.02 (Table 1), which was comparable with the values of K_f 2.62–3.10 or 3.13–3.44 about adsorption E2 using activated sludge or aerobic granular sludge, respectively [19]. The constant is an empirical parameter associated with the degree of heterogeneity. A higher value of means a stronger heterogeneity [39,40], indicating a higher probability for E2 to combine with AnGS. The 0.82 value of (close to 1) reflected high adsorption intensity between AnGS and E2. Taken together, the high and values demonstrate that E2 can be effectively removed by AnGS through adsorption.

3.4. Adsorption thermodynamic

Thermodynamic behavior of E2 adsorption by AnGS was investigated at different temperatures. The values of K_d were calculated by Eq. (7) according to above experimental data. Drawing a straight line of ln-K_c against 1/T, $\Delta H°$ and $\Delta S°$ were calculated according the slope and intercepts of the fitting equation about the straight line (Fig. 8). The high R^2 coefficient value (0.954) of the fitting equation suggested the accuracy of $\Delta H°$ and $\Delta S°$ in Eq. (8). The values of $\Delta H°$ and $\Delta S°$ were –22.3 KJ·mol^{-1} and –19.7 J·mol^{-1}·K^{-1}, respectively. The $\Delta H°$ value is close to the values of –31.3 KJ·mol^{-1} and –37.42 KJ·mol^{-1} reported by Zheng et al. [19] who studied E2 adsorption by activated sludge and aerobic granular sludge. The negative value of $\Delta H°$ indicated that E2 adsorption process by AnGS was exothermic. Further, lower temperature was more conducive to E2 adsorption removal.

Adsorption process was mainly dominated by chemical adsorption at $\Delta H° > -60$ KJ·mol^{-1}, or by physical adsorption at $\Delta H° < -40$ KJ·mol [41]. Estrogen adsorption by AnGS was mainly dominated by physical adsorption ($\Delta H° = -22.3$ KJ·mol^{-1}). The negative value of $\Delta S°$ suggests a more regular state of adsorbate over adsorbent surfaces [42]. The values of $\Delta G°$ at different temperatures were calculated by Eq. (9) and were listed in Table 2. The value of $\Delta G°$ was negative and increased as temperature increased. This negative value of $\Delta G°$ suggested E2 adsorption process by AnGS was spontaneous. The adsorption of E2 by AnGS was a physical adsorption accompanying with spontaneous heat release.

Table 1
Adsorption parameters and correlation coefficients for different isotherm models

Adsorption isotherm model	Parameter	R^2
Freundlich $q_e = K_f C_e^{1/n}$	$K_f = 1.02$ $n = 0.82$	0.994
Langmuir $q_e = \dfrac{q_{\max} \cdot b \cdot C_e}{1 + b \cdot C_e}$	$q_{max} = 14.2$ $b = 0.07$	0.992
Tempkin $q_e = \mathrm{B} \cdot \ln q_e + \mathrm{B} \cdot \ln A$	A =1.73 B = 1.68	0.929

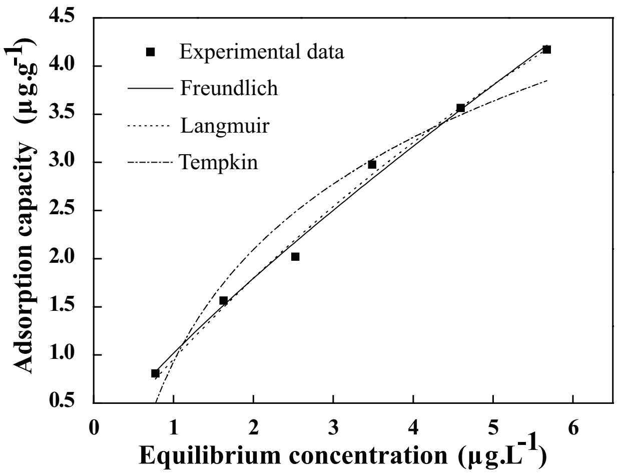

Fig. 7. Isotherm plots for the adsorption of E2 by AnGS.

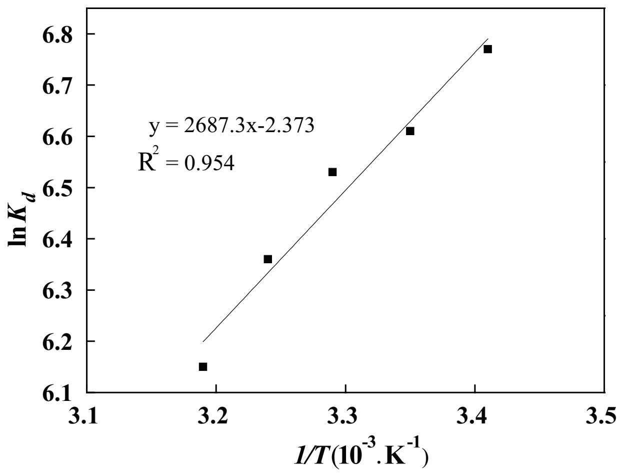

Fig. 8. Thermodynamic plot for the adsorption of E2 by AnGS.

Table 2
Thermodynamic parameters of adsorption E2 by AnGS at different temperatures

T(K)	$\Delta G°$	$\Delta H°$	$\Delta S°$
293.5	–16.52	–22.3	–19.7
298.5	–16.41	–22.3	–19.7
303.5	–16.32	–22.3	–19.7
308.5	–16.22	–22.3	–19.7
313.5	–16.12	–22.3	–19.7
318.5	–16.03	–22.3	–19.7

Table 3
Kinetic constant for pseudo-first-order and pseudo-second-order model

C_0	The pseudo-first-order			The pseudo-second-order			$q_{e,exp}$
	$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	R^2	
2	0.48	0.081	0.913	0.93	0.41	0.999	0.90
4	1.03	0.092	0.957	1.81	0.34	0.999	1.78
6	1.78	0.106	0.965	2.67	0.34	0.997	2.65
8	2.22	0.080	0.894	3.44	1.29	0.994	3.51
10	2.85	0.082	0.899	3.90	1.31	0.991	3.99

The exothermic nature of E2 adsorption and the increased $\Delta G°$ value explained why AnGS adsorption capacity and E2 adsorption removal efficiency both decreased as temperature increased.

3.5. Adsorption kinetics

A rapid adsorption rate is desirable for adsorption processes. Adsorption kinetic models can be used to determine the adsorption rate and evaluate the availability of adsorbent. Three kinetic models (pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model) were used to describe the adsorption data at different initial E2 concentration to evaluate the adsorption rate and adsorption dynamics mechanism of E2 adsorption by AnGS.

3.5.1. Pseudo-first-order and pseudo-second-order models

The pseudo-first-order and pseudo-second-order models were used to describe the experiment data. The values of correlation coefficient R^2 about pseudo-first-order model were between 0.889 and 0.989. The values of correlation coefficient R^2 about the pseudo-second-order model ranged from 0.991 to 0.999. The R^2 values of the pseudo-second-order model were higher than those of the pseudo-first-order model.

The values of adsorption capacity (q_e) and adsorption rate constant (k_1,k_2) in Eqs. (10) and (11) were calculated according to the slope and intercepts of straight line plots of lg(q_e – q_t) or t/q_t vs t. All parameter values, including the theoretical adsorption capacity ($q_{e,cal}$) and the experimental adsorption capacity ($q_{e,exp}$), were summarized and listed in Table 3. The values of calculated with Eq. (10) were far from the values. The values of $q_{e,cal}$ calculated by Eq. (11) were closer to the $q_{e,exp}$ values. The higher R^2 values and similar $q_{e,cal}$ and $q_{e,exp}$ values prove that the pseudo-second-order model was better suited to describing E2 adsorption process by AnGS compared with the pseudo-first-order model.

When initial E2 concentration increased from 2 μg·L^{-1} to 10μg·L^{-1}, the values of increased from 0.93 μg·g^{-1} to 3.90 μg·g^{-1}. The values of changed only slightly with initial E2 concentration rising from 2 μg·L^{-1} to 6 μg·L^{-1}, but then rapidly increased as E2 concentration continue increased (Table 3). This jump from 0.34 g.μg^{-1}.min^{-1} to 1.29 g.μg^{-1}.min^{-1} may have been due to overcoming mass transfer resistance resulted by an increase in initial E2 concentration from 6 μg·L^{-1} to 8 μg·L^{-1}. Higher E2 concentration provided a higher mass transfer driving force and overcame the mass transfer resistance in the film diffusion and intraparticular diffusion processes [43], which promoted a rise in the adsorption rate and increased adsorption removal of E2 by AnGS.

The pseudo-second-order model basically includes all steps of adsorption such as external film diffusion, intraparticle diffusion, and adsorption reaction. The step of adsorption reaction is always considered to be rapid and to be negligible. Hence, the overall adsorption rate was controlled by film diffusion or intraparticle diffusion.

3.5.2. Intraparticle diffusion model

The intraparticle diffusion resistance was investigated by using the intraparticle diffusion model (Eq. (12)) [43]. The plots of q_t vs $t^{1/2}$ were determined using Eq. (12) with the experiment data at different points of initial E2 concentration, as shown in Fig. 9. The values of K_3 and C in Eq. (12) were calculated according to the slope and intercepts of plots in Fig. 9, as listed in Table 4. The correlation coefficient values of R^2 ranged from 0.947 to 0.997. The high R^2 values proved that the intraparticle diffusion model described the experiment data well.

The adsorption equilibriums under different initial E2 concentrations were reached at 40 min (Fig. 2). Hence, the values for q_t and $t^{1/2}$ were all within 40 min and were shown in three regions in Fig. 9. The first region with the $t^{1/2}$ between 10 and 20 min was due to the diffusion of E2 from the solution to the external surface of AnGS or the boundary layer diffusion of E2 molecules [34]. The second region with the $t^{1/2}$ between 25 min and 35 min described a stage of further adsorption where intraparticle diffusion occurred with a rate-limiting step. The third region (only shown as a data point) was due to the equilibrium stage for which intraparticle diffusion started to slow down due to a lack of E2 in the solution. The linear plots of the second region did not pass through the origin, indicating that intraparticle diffusion was not the only rate-limiting step [43]. The overall adsorption process of E2 by AnGS was controlled by film diffusion and intraparticle diffusion.

When initial E2 concentration increased from 2 μg·L^{-1} to 10 μg·L^{-1}, the values of k_3 increased from 0.151 g.μg$^{-1/2}$. min^{-1} to 0.415 g·μg$^{-1/2}$.min^{-1} in the first region and further increased from 0.017 g·μg$^{-1/2}$·min^{-1} to 0.192 g·μg$^{-1/2}$·min^{-1} in the second region. The rise in k_3 values may be attributed to a greater driving force with the increase of initial E2 concentration. High E2 concentration stimulated the E2 diffusion

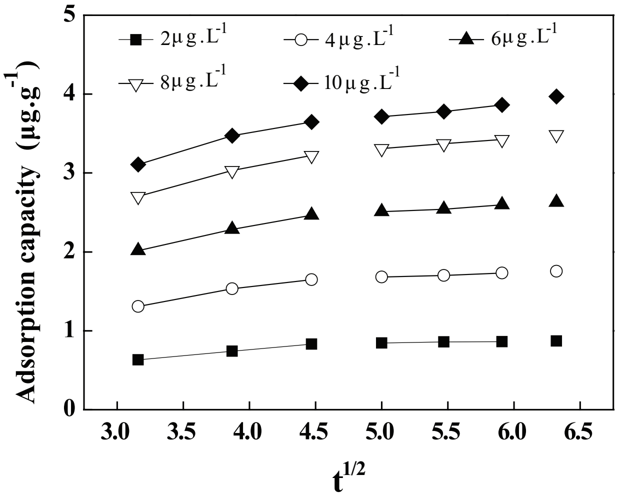

Fig. 9. Intraparticle diffusion plots for the adsorption of E2 by AnGS.

Table 4
Intraparticle diffusion constant of adsorption E2 by AnGS

C_0	The first region			The second region		
	k_3	C	R^2	k_3	C	R^2
2	0.151	0.155	0.889	0.017	0.764	0.947
4	0.261	0.493	0.981	0.057	1.393	0.988
6	0.344	0.936	0.985	0.092	2.046	0.984
8	0.398	1.459	0.989	0.133	2.639	0.997
10	0.415	1.819	0.976	0.192	2.738	0.978

in the AnGS pores and enhanced the intraparticle diffusion rate. The values of k_3 in the first region were much larger than those in second region, suggesting that the adsorption of E2 by AnGS proceeded rapidly in the initial stage.

4. Conclusions

1 E2 can be effectively removed by AnGS adsorption at a removal efficiency of 60.54%.
2 E2 adsorption removal by AnGS was a fast adsorption process. E2 removal efficiency and AnGS adsorption capacity for E2 increased with initial E2 concentration ranging from 2 μg·L^{-1} to 12 μg·L^{-1}. With a rise in AnGS concentration, adsorption capacity decreased gradually and E2 removal efficiency first increased and then decreased.
3 Low pH and low temperature led to a better adsorption removal of E2 by AnGS. NaCl played a promoted role in the adsorption process at lower ionic strength.
4 The Freundlich isotherm was suitable to describe E2 adsorption process by AnGS. Thermodynamic studies indicated that E2 adsorption by AnGS was a physical adsorption process accompanying with spontaneous heat release.
5 The pseudo-second-order model was proven appropriate for describing E2 adsorption kinetics process by AnGS. The overall adsorption process was controlled by film diffusion and intraparticle diffusion. Kinetic analysis indicated that the adsorption rate increased as E2 concentration increased

Acknowledgements

The authors gratefully acknowledge the funding of the National Natural Science Foundation of China (51308010), Scientific Research Project of Beijing Educational Committee (KM201210005028), and Research Fund for the Doctoral Program of Higher Education of China (20131103120017).

References

[1] A.Y.C. Lin, Y.T. Tsai, T.H. Yu, X.H. Wang, C.F. Lin, Occurrence and fate of pharmaceuticals and personal care products in Taiwan's aquatic environment, Desal. Water Treat., 32 (2011) 57–64.
[2] J.Y. Hu, S.J. Cheng, T. Aizawa, Y. Terao, S. Kunikane, Products of aqueous chlorination of 17 beta-estradiol and their estrogenic activities, Environ. Sci. Technol., 37 (2003) 5665–5670.
[3] S. Itoh, H. Ueda, T. Naasaka, G. Nakanishi, H. Sumitomo, Evaluating variation of estrogenic effect by drinking water chlorination with the MVLN assay, Water Sci. Technol., 42 (2000) 61–69.
[4] A.C. Johnson, R.J. Williams, A model to estimate influent and effluent concentrations of estradiol, estrone, and ethinylestradiol at sewage treatment works, Environ. Sci. Technol., 38 (2004) 3649–3658.
[5] X.Y. Ma, K. Tang, Q.S. Li, Y.L. Song, Y.J. Ni, N.Y. Gao, Degradation of 17 beta-estradiol by combined ultrasound/$KMnO_4$ in an aqueous system, Desal. Water Treat., 53 (2015) 493–500.
[6] Y.M. Li, Q.L. Zeng, S.J. Yang, Removal and fate of estrogens in an anaerobic-anoxic-oxic activated sludge system, Water Sci. Technol., 63 (2011) 51–56.
[7] Z.H. Zhang, Y.J. Feng, H. Su, L.J. Xiang, Q.Y. Zou, P. Gao, P.R. Zhan, Influence of operating parameters on the fate and removal of three estrogens in a laboratory-scale AAO system, Water Sci. Technol., 71 (2015) 1701–1708.
[8] M.J. Lust, R.M. Ziels, S.E. Strand, H.L. Gough, H.D. Stensel, Biodegradation kinetics of 17 alpha-ethinylestradiol in activated sludge treatment processes, Environ. Eng. Sci., 32 (2015) 637–646.
[9] D. Belhaj, I. Jaabiri, H. Ayadi, M. Kallel, J.L. Zhou, Occurrence and removal of steroidal estrogens in Centre Eastern Tunisia municipal sewage treatment plant, Desal. Water Treat., 52 (2014) 2330–2339.
[10] S. Dagnino, B. Picot, A. Escande, P. Balaguer, H. Fenet, Occurrence and removal of endocrine disrupters in wastewater treatment plants for small communities, Desal. Water Treat., 4 (2009) 93–97.
[11] O.T. Komesli, M. Muz, M.S. Ak, S. Bakirdere, C.F. Gokcay, Occurrence, fate and removal of endocrine disrupting compounds (EDCs) in Turkish wastewater treatment plants, Chem. Eng. J., 277 (2015) 202–208.
[12] X.H. Yu, J.C. Xue, H. Yao, Q. Wu, A.K. Venkatesan, R.U. Halden, K. Kannan, Occurrence and estrogenic potency of eight bisphenol analogs in sewage sludge from the US EPA targeted national sewage sludge survey, J. Hazard. Mater., 299 (2015) 733–739.
[13] L. Gonzalez-Gil, M. Papa, D. Feretti, E. Ceretti, G. Mazzoleni, N. Steimberg, R. Pedrazzani, G. Bertanza, J.M. Lema, M. Carballa, Is anaerobic digestion effective for the removal of organic micropollutants and biological activities from sewage sludge?, Water Res., 102 (2016) 211–220.

[14] O. Bergersen, K.O. Hanssen, T. Vasskog, Anaerobic treatment of sewage sludge containing selective serotonin reuptake inhibitors, Biores. Technol., 117 (2012) 325–332.

[15] V.M. Monsalvo, J.A. McDonald, S.J. Khan, P. Le-Clech, Removal of trace organics by anaerobic membrane bioreactors, Water Res., 49 (2014) 103–112.

[16] T.Z.D.D. Mes, K. Kujawa-Roeleveld, G. Zeeman, G. Lettinga, Anaerobic biodegradation of estrogens - hard to digest, Water. Sci. Technol., 57 (2008) 1177–1182.

[17] M. Carballa, F. Omil, T. Ternes, J.M. Lema, Fate of pharmaceutical and personal care products (PPCPs) during anaerobic digestion of sewage sludge, Water Res., 41 (2007) 2139–2150.

[18] A. Chiavola, P. Tedesco, M.R. Boni, Fate of some endocrine disruptors in batch experiments using activated and inactivated sludge, Water Air Soil Poll., 227 (2016) 424.

[19] X.Y. Zheng, Y.J. He, W. Chen, M.Y. Wang, S.L. Cao, M. Ni, Y. Chen, A comparative adsorption study: 17 beta-estradiol onto aerobic granular sludge and activated sludge, Environ. Technol., 37 (2016) 136–144.

[20] Q.L. Zeng, Y.M. Li, G.W. Gu, Nitrate-dependent degradation of 17 alpha-ethinylestradiol by acclimated activated sludge under anaerobic conditions, J. Chem. Technol. Biot., 84 (2009) 1841–1847.

[21] J.C. Li, S.J. Yuan, W. Wang, F. Ji, Z.H. Hu, Adsorption characteristics of 4-hydroxy-3-aminophenylarsonic acid (HAPA) onto anaerobic granular sludge, Desal. Water Treat., 57 (2016) 20714–20725.

[22] X.F. Sun, S.G. Wang, W. Cheng, M.H. Fan, B.H. Tian, B.Y. Gaó, X.M. Li, Enhancement of acidic dye biosorption capacity on poly(ethylenimine) grafted anaerobic granular sludge, J. Hazard. Mater., 189 (2011) 27–33.

[23] L. Shi, D. Wei, H.H. Ngo, W.S. Guo, B. Du, Q. Wei, Application of anaerobic granular sludge for competitive biosorption of methylene blue and Pb(II): Fluorescence and response surface methodology, Biores. Technol., 194 (2015) 297–304.

[24] X.Y. Ma, K. Tang, Q.S. Li, Y.L. Song, Y.J. Ni, N.Y. Gao, Parameters on 17 beta-Estradiol degradation by Ultrasound in an aqueous system, J. Chem. Technol. Biot., 89 (2014) 322–327.

[25] J.P. Bassin, M. Pronk, R. Kraan, R. Kleerebezem, M.C.M. van Loosdrecht, Ammonium adsorption in aerobic granular sludge, activated sludge and anammox granules, Water Res., 45 (2011) 5257–5265.

[26] V.O. Njoku, K.Y. Foo, M. Asif, B.H. Hameed, Preparation of activated carbons from rambutan (Nephelium lappaceum) peel by microwave-induced KOH activation for acid yellow 17 dye adsorption, Chem. Eng. J., 250 (2014) 198–204.

[27] V.J.P. Vilar, C.M.S. Botelho, R.A.R. Boaventura, Equilibrium and kinetic modelling of Cd(II) biosorption by algae Gelidium and agar extraction algal waste, Water Res., 40 (2006) 291–302.

[28] M.L. Paul, J. Samuel, N. Chandrasekaran, A. Mukherjee, Comparative kinetics, equilibrium, thermodynamic and mechanistic studies on biosorption of hexavalent chromium by live and heat killed biomass of Acinetobacter junii VITSUKMW2, an indigenous chromite mine isolate, Chem. Eng. J., 187 (2012) 104–113.

[29] J. Zhang, G.P. Yang, Q. Li, X.Y. Cao, G.X. Liu, Study on the sorption behaviour of estrone on marine sediments, Mar. Pollut. Bull., 76 (2013) 220–226.

[30] A.H. Sulaymon, D.W. Abbood, A.H. Ali, A comparative adsorption/biosorption for the removal of phenol and lead onto granular activated carbon and dried anaerobic sludge, Desal. Water Treat., 51 (2013) 2055–2067.

[31] X.L. Yang, L. Liang, H.L. Song, Y.C. Gao, S.B. Huang, B.L. Dai, Adsorption of estrone by selected constructed wetland substrates, Fresen. Environ .Bull., 24 (2015) 291–301.

[32] Z. Aksu, A.B. Akin, Comparison of Remazol Black B biosorptive properties of live and treated activated sludge, Chem. Eng. J., 165 (2010) 184–193.

[33] M. Horsing, A. Ledin, R. Grabic, J. Fick, M. Tysklind, J.L. Jansen, H.R. Andersen, Determination of sorption of seventy-five pharmaceuticals in sewage sludge, Water Res., 45 (2011) 4470–4482.

[34] Z. Aksu, A.I. Tatli, O. Tunc, A comparative adsorption/biosorption study of Acid Blue 161: Effect of temperature on equilibrium and kinetic parameter, Chem. Eng. J., 142 (2008) 23–39.

[35] M. Clara, B. Strenn, E. Saracevic, N. Kreuzinger, Adsorption of bisphenol-A, 17 beta-estradiole and 17 alpha-ethinylestradiole to sewage sludge, Chemosphere, 56 (2004) 843–851.

[36] M. Gorgenyi, J. Dewulf, H. Van Langenhove, K. Heberger, Aqueous salting-out effect of inorganic cations and anions on non-electrolytes, Chemosphere, 65 (2006) 802–810.

[37] S.K. Das, P. Ghosh, I. Ghosh, A.K. Guha, Adsorption of rhodamine B on Rhizopus oryzae: Role of functional groups and cell wall components, Colloid Surface B, 65 (2008) 30–34.

[38] E.R. Alley, Water quality control handbook, 2nd ed., McGraw-Hill, WEF Press, New York. Alexandria, Va., 2007.

[39] C. Nguyen, D.D. Do, The Dubinin-Radushkevich equation and the underlying microscopic adsorption description, Carbon, 39 (2001) 1327–1336.

[40] H. Chen, G.L. Dai, J. Zhao, A.G. Zhong, J.Y. Wu, H. Yan, Removal of copper(II) ions by a biosorbent-Cinnamomum camphora leaves powder, J. Hazard. Mater., 177 (2010) 228–236.

[41] B. Vonoepen, W. Kordel, W. Klein, Sorption of nonpolar and polar compounds to soils - processes, measurements and experience with the applicability of the modified Oecd-Guideline-106, Chemosphere, 22 (1991) 285–304.

[42] M. Cekim, S. Yildiz, T. Dere, Biosorption of copper from synthetic waters by using tobacco leaf: equilibrium, kinetic and thermodynamic tests, J. Environ. Eng. Landsc., 23 (2015) 172–182.

[43] M. Arami, N.Y. Limaee, N.M. Mahmoodi, Evaluation of the adsorption kinetics and equilibrium for the potential removal of acid dyes using a biosorbent, Chem. Eng. J., 139 (2008) 2–10.