Equilibrium and kinetic of aniline adsorption onto crosslinked sawdust-cyclodextrin polymers

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Abstract

A natural origin adsorbent was made by sawdust and beta-cyclodextrin (β-CD) for removal of the organic (aniline) during water pollution accidents. β-CD attaches on the sawdust surface and forms an organic film based on the results of BET, SEM and FTIR. Batch tests show that the optimum pH for aniline adsorption is in the range of 4-8. Adsorption equilibrium is achieved in about 30 minutes, and the adsorption kinetic follows a pseudo-second-order kinetic model. The Langmuir model appears to fit the isotherm data better than the Freundlich model at 15 °C compared with 30 °C and 45 °C. And the maximum adsorption capacity is estimated to be 84.03 mg/g at 15 °C (R^2>0.99). The negative value of standard entropy ($\triangle H^o$) and standard free energy ($\triangle G^o$) indicate the exothermic and spontaneous nature of the adsorption interaction. Moreover, the results of FTIR suggest that the formation of an inclusion complex between the β-CD and aniline molecules through host-guest interactions enhances adsorptive capability.

Keywords: Cyclodextrin; Sawdust; Aniline adsorption; Isotherms; Emergency

1. Introduction

In China, malignant water pollution accident occurs frequently with the development of modern industry. According to the statistics, there were 1176 malignant water pollution accidents from 2000 to 2011, many of which threatened the safety of water sources.[1] Among these accidents, the pollution of the organic has attracted much attention. One particularly serious event was the Nitrobenzene Spill in the Songhua River in 2005, which caused Harbin, the capital of Heilongjiang Province, had to cut off its water supply for 4 days.[2] Another serious accident happened in December 2012, about 8.7 tons of aniline leaked into the Zhuozhang River, and the water supply of Handan City was cut off, which made more than one million people lack of adequate drinking water.[3] It is a challenge to provide safety drinking water during an emergency due to inadequate access to infrastructure. Hence, emergency water technologies, which are modular, mobile or portable, are appropriate for in-situ remediation as they can provide a location-specific solution.[4]

The adsorption technology, which has been used in the emergency response,[2] has the characters of high efficiency, ease of construction and operation, and coordination with conventional processes. Activated carbon is widely used adsorbent and has the capacity to adsorb a wide range of pollutants.[5] However, it is still facing some problems such as high costs, requiring complex agents to improve adsorption capacity, non-selectiveness and having problems with hydrophilic substances.[6,7] Therefore, in recent years, various alternative adsorbents have been developed for pollution removal using natural or synthetic polymers such as chitosan,[8,9] sawdust,[10-12] cyclodextrins etc. [13-16].

Beta-cyclodextrin (β-CD) is the most largely produced cyclodextrin used in many fields including pharmaceuticals, foods, chemical products and technologies.[17] It is torus-shaped cyclic oligosaccharide containing 6-12 glucose units. The structure of β-CD makes it ease to form inclusion complexes with organic molecules, through a host-guest interaction.[14] Numerous approaches have been studied in the development of cheaper and more effective adsorbents containing β-CD.[13-15,18,19] It is a good choice to use β-CD-based material toward organic molecules based on the related researches.[14,15,20] β-CD-based polymers using epichlorohydrin (EPI) as a cross-linking agent is a most straight forward method.[19,21] However, the main disadvantage of EPI is its toxicity, which is neither safe nor environmentally friendly.[14] Water insoluble β-CD polymer crosslinked by eco-friendly' agent such as polycarboxylic acids was obtained by literature,[22] and the material exhibited well in environmental protection. The environmentally benign character makes this method suitable for preparation of adsorbent. And a simplified process and a mild reaction condition may make the adsorbent ideally suited for emergency response.

Aniline, an oily and colorless liquid, is a highly acrid poison. It is frequently used in the manufacture of dyes, rubbers, pharmaceutical preparation, plastic and paint. As an important organic chemical raw material, aniline is a kind of potential source of risk, and its presence, even in very low concentrations, has been shown to be harmful to aquatic life.[23] In fact, wastewater containing aniline discharged from these industries has become a severe environmental problem as well. A rapid and effective method should be developed to remove it from industrial wastes. So the information is important about β-CD-based polymer for the sorption of aniline.

On this basis, this study was conducted to assess the adsorptive capacity of a sawdust-β-CD polymer (SD-β-CD) for aniline. In order to improve the preparation efficiency, a simplified and green making process was used. The effects of several parameters such as pH, kinetics and temperature are evaluated and discussed to explore the adsorption properties. The adsorption mechanism of aniline onto sawdust-β-CD polymer is investigated through BET, SEM and FTIR analyses. In addition, the equilibrium data have been analyzed using Freundlich and Langmuir isotherms, and the characteristic's parameters for each isotherm have been determined.

2. Materials and methods

2.1. Preparation of sawdust-β-cyclodextrin polymer (SD-β-CD)

The following materials were used for fabricating SD-β-CD: sawdust (60-80 mesh) was rinsed thoroughly with deionized water and then dried at 105 °C for 24 h; beta-cyclodextrin (β-CD), citric acid (CA), and the catalyst of NaH_2PO_4. Aniline was purchased from Shanghai Chemical Reagent Co., China; Stock solutions of aniline were prepared using deionized water. All reagents were of analytical grade and used as received without further purification.

SD-β-CD was prepared according to the following procedures: a mixture of sawdust

(2 g), β-CD (5 g), CA (3 g) and NaH_2PO_4 (0.5 g) in deionized water (50 mL) were performed under sonic oscillation for 20 minutes. CA was the crosslinking agent. And the mixture was cured at 160 °C for 15 minutes. The obtained solid was sufficiently washed through stirring and washing by warm water and alcohol alternately. Finally, the sample was dried at 105 °C. After purified and dried, SD-β-CD was obtained as dark beige crisp granular with a yield of 7.6 g. At the end of reaction, the content of insoluble matter is increased from 19.0% (sawdust) to 72.4% (SD-β-CD). SD, β-CD and CA carried on esterification reaction catalyzed by NaH_2PO_4. CA modified sawdust (CASD) was prepared at the same process but without β-CD.

2.2. Characterization of sawdust-β-cyclodextrin polymer (SD-β-CD)

The surface morphology of SD-β-CD was examined by scanning electron microscopy (S-570, Japan). Fourier transform infrared (FTIR) spectroscopy measurements were conducted with UV2550 (Shimadzu Co., Ltd., Japan) using KBr as background over the range of 4000–450cm^{-1}. The BET surface area and porosity of the samples were determined by accelerated surface area and Porosometry system (ASAP 2020, Global Spec. Inc., US).

2.3. Adsorption kinetics

Aniline adsorption kinetic experiment was performed in 250 mL flasks using 0.20 g adsorbents, and the solution was 100 mL with a adjusted pH of 7.0. The initial concentration was 17 and 85 mg/L, and the solution was shaken at 135 rpm (15 °C). 1 mL samples were taken from the suspension at certain intervals, which were filtered through a 0.45 mm glass fiber membrane prior to analysis. And the absorbance of aniline was measured at 545 nm using a UV-Vis dual-beam spectrophotometer (T6, China).

The amount of adsorptions at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

Where C_o (mg/L) is the initial concentration, and C_t (mg/L) is the real-time concentrations of aniline in liquid phase; q_t (mg/g) is the amount of aniline absorbed by SD-β-CD; V (L) is the volume of solution, and m (g) is the mass of dry adsorbent used.

The kinetic data were then fitted using the pseudo-first-order (2) and pseudo-second-order (3) models, respectively:[24,25]

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Where q_e (mg/g) and q_t (mg/g) are the amounts of aniline adsorbed at equilibrium and at time t (min), respectively; k_1 (1/min) and k_2 [g/(mg•min)] are the corresponding rate constants.

2.4. Adsorption isotherms

Isothermal adsorption experiment was conducted in a batch of Erlenmeyer flasks (250 mL) where 100 mL of aniline solutions with initial concentrations of 20-1200 mg/L were placed in these flasks. The adsorbents (0.50 g) were added to each flask and kept in an isothermal shaker of 135 rpm at 15 °C for 24 h to reach equilibrium. The pH was adjusted to 7.0 using NaOH (0.1 mol/L) and HNO_3 (0.1 mol/L). Similar thermodynamic studies were followed for another two sets of Erlenmeyer flasks containing the same initial aniline concentrations and adsorbents dosage, but were kept at 30 and 45 °C, respectively. In order to minimize interference of the polymers' fines with the analysis, each sample was filtered prior to analysis.

The equilibrium data are fitted by Langmuir and Freundlich isotherm equations. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites.[26] The linear form of Langmuir equation can be expressed as:

$$\frac{C_e}{q_e}=\frac{1}{q_{max}K_l}+\frac{C_e}{q_{max}} \quad (4)$$

Where C_e (mg/L) is the equilibrium concentration in solution, q_e (mg/g) is the amount of adsorbed material at equilibrium; q_{max} (mg/g) is the maximum capacity of adsorbent, and K_L (L/g) is the Langmuir isotherm constant.

The Freundlich isotherm is an empirical equation, which suggests that sorption energy exponentially decrease on completion of the sorptional centres of an adsorbent.[27] The linear form of Freundlich equation is expressed as follows:

$$lnq_e=lnK_F+\frac{1}{n}lnC_e \quad (4)$$

Where q_e (mg/g) is the equilibrium adsorbate concentration on adsorbent, C_e (mg/L) is the equilibrium adsorbate concentration in solution, K_F [(mg/g)(L/mg)$^{1/n}$] is Freundlich constant, and $1/n$ is the heterogeneity factor. The capacity constant K_F and the affinity constant n are empirical constants dependent on several environmental factors. A value for *1/n* below one can be defined a normal Langmuir isotherm while *1/n* above one is indicative of cooperative adsorption.[28]

3. Results and discussion

3.1. Characterization of sawdust-β-cyclodextrin polymer (SD-β-CD)

The N_2 adsorption-desorption isotherms of SD-β-CD (or raw sawdust) is similar to type II with H_1 hysteresis loop (Fig. 1), according to IUPAC classification. The BET surface area and total pore volume of the SD-β-CD (0.11 m^2/g, 1.18×10^{-4} cm^3/g) are both smaller than raw sawdust (0.72 m^2/g, 8.85×10^{-4} cm^3/g). In fact, for either β-CD or sawdust, the specific surface areas are in general extremely low compared to that of porous adsorbents like CAC (1100 m^2/g) or commercial synthetic zeolite (450 m^2/g).[29,30] Although the surface area of the β-CD based polymers varied based on different starting materials and different methods, similarly small specific surface area (0.11-8.01 m^2/g) was observed in some studies.[15,31,32] The surface area is not the factor for SD-β-CD to adsorb aniline as the adsorption mechanism of β-CD to organic molecules is completely different from porous materials.

Both the raw sawdust and citric acid modified sawdust (CASD) have a rough surface, whereas SD-β-CD is covered by an organic film and has a rather smooth surface (Fig. 2). The β-CD film coats the entire surface of sawdust and is successfully grafted on sawdust. It is the coverage of organic film that makes the surface area of SD-β-CD smaller than raw sawdust. The adsorption capacity of SD-β-CD was improved significantly ($q_{max,\ raw\ sawdust}$<10 mg/g, $q_{max,\ SD\text{-}\beta\text{-}CD}$>80 mg/g, $q_{max,\ raw\ sawdust}$<$q_{max,}$

${}_{CASD}<q_{max,\ SD\text{-}\beta\text{-}CD}$, 15 °C). It is reported that β-CD-polymer may be easily swelled in water because the β-CD had many hydrophilic groups.[22] In terms of SD-β-CD, due to β-CD matrix on the surface, most aniline molecules which are not easily fixed on sawdust would be entrapped or attached by SD-β-CD.

The grafting of β-CD on surfaces of sawdust was confirmed by an FTIR spectroscopy (Fig. 3). The intensive absorption band appears at 1735cm^{-1} in SD-β-CD spectrum(d), which is owed to C=O stretching vibration of carboxyl groups and ester groups. The peak at 1207 cm^{-1} in (d) is assigned to C–O–C stretching vibration of ester groups, which is absent in sawdust spectrum (b), β-CD spectrum (a) and the mixture (e). The two bands observed in (d) indicate that the hydroxyl groups of sawdust and β-CD have reacted with the carboxyl groups of citric acid. The esterification reaction happens between citric acid and β-CD, both of them have a higher reactivity than sawdust. The adsorption capacity of sawdust, CASD, SD-β-CD and CA crosslinked β-cyclodextrin is 1.2, 13.2, 16.3 and 17.8 mg/g at 100 mg/L aniline solution (15 °C). It is not surprising that CA crosslinked β-cyclodextrin without sawdust performs better than the ones with sawdust. But the SD-β-CD shows a good adsorption property compared with CA crosslinked β-cyclodextrin. This is mainly because citric acid modified sawdust (CASD) can also improve the adsorption property. The intensive absorption band appears at 1735cm^{-1} in (c) can explain the increased adsorption capacity of CASD. The presence of transesterification between sawdust and citric acid is clear. This process can reduce the amount of β-CD used in the SD-β-CD. And the citric acid is a bridge to link sawdust and β-CD for SD-β-CD.

3.2. Adsorption of aniline onto sawdust-β-cyclodextrin polymer (SD-β-CD)

3.2.1 Effect of initial pH

The initial pH of adsorption was evaluated in the pH range of 2-10 (Fig. 4). The adsorption capacity reached a minimum at 2.6, and then increased with pH up to 4 and remained approximately unchanged from pH 4-8. When the pH exceeded 8, the adsorption capacity of SD-β-CD decreased obviously. Hence, the absorption can proceed under faintly acid and neutral conditions. In fact, SD-β-CD exhibits moderate acidity in aqueous solution as the cross-linking agent is citric acid. The equilibrated adsorption capacity was between 14.6 and 15.0 mg/g, which showed stable adsorption ability in weak acidic medium. The sorption amount decreased rapidly at high pH, which can be explained by the acidity of citric acid. Citric acid is a bridge between the sawdust and β-CD, and the stability of ester bond between sawdust and β-CD can be affected by extreme alkalinity. Adsorption capacity decreased when the pH dropped below 4. At sufficiently high acidity, β-CD may be hydrolyzed to glucose and maltose. The peculiar hydrophobic cavum of β-CD is broken, so the aniline cannot be incorporated into the β-CD ring. In fact, SD-β-CD is a mixture of citric acid modified sawdust (CASD) and SD-β-CD. The adsorption of aniline by CASD is more like electrostatic forces, and the acid and base attraction lead to a response to pH. Besides, aniline is in the form of molecular at pH 7-10, and NH_2 becomes a activate group.[33] An alkaline condition may make OH^- ions compete effectively with NH_2 for the bonding sites of adsorbent.

3.2.2 Adsorption kinetics

The adsorption capacity of SD-β-CD versus the contact time was investigated at two concentrations (17 and 85 mg/L) at 15 °C (Fig.5a). The adsorption process was fast and equilibrium reached in about 30 minutes. The adsorption capacity increased with initial aniline concentration (Fig.5a). Kinetic models were used to describe the process to find the adsorption order. The pseudo-first-order kinetic equation was tested firstly, but the linear relation could not be obtained. Then the data was analyzed by pseudo-second-order model, and t/q_t versus t graphs were calculated (Fig.5b). Results indicates that the pseudo-second-order model fits the adsorption kinetics well (>99%). The q_e (the amounts of aniline adsorbed at equilibrium) values calculated from the pseudo second-order model ($q_{e,cal}$) are consistent with the experimental values ($q_{e,exp}$). For a higher initial concentration (85 mg/L), $q_{e,exp}$=12.99 mg/g, $q_{e,cal}$=13.39 mg/g, k_2=0.0056 g/(mg·min), and R^2=0.9985. When the initial concentration was 17 mg/L, $q_{e,exp}$=4.02 mg/g, $q_{e,cal}$=4.16 mg/g, k_2=0.0578 g/(mg·min), and R^2=0.9992. So the adsorption kinetic is described by the pseudo-second-order model. Similar results have been reported in adsorption of C.I.Basic Blue 9 on a cyclodextrin polymer[27] and copper ions on Carboxymethyl-β-cyclodextrin.[34]

3.2.3 Adsorption isotherms

Adsorption isotherms indicate how the pollutant interacts with sorbent when the adsorption process reaches an equilibrium state. And some important information on the adsorption mechanism can be obtained from the parameters. The equilibrium isotherm of SD-β-CD was compared at different temperatures (15, 30 and 45 °C) (Fig.6a). Langmuir and Freundlich isotherm equations were applied to fit the data (Fig.6b, 6c), and isotherm parameters were calculated and summarized. From the Langmuir isotherm, the maximum adsorption capacity is 84.0, 75.2 and 64.1 mg/g at 15, 30 and 45 °C, respectively, and correlation coefficients (R^2) is 0.9904, 0.9649 and 0.9551, correspondently. The results reveal that SD-β-CD possesses strong adsorption ability for aniline. From the Freundlich isotherm, the affinity constant n is 0.70, 0.63 and 0.57 at 15, 30 and 45 °C separately, and the R^2 is 0.9793, 0.9934 and 0.9952 correspondently. Freundlich type isotherm can be a good description of the adsorption behavior.

The applicability of the isotherms for the adsorption process can be judged by R^2. From the R^2 values, the Langmuir isotherm (R^2>0.99) shows a better fit to experimental data than the Freundlich (R^2>0.97) at 15 °C. The linear regression line of the Langmuir has a low significant R^2 value (R^2<0.99) as the temperature rises. The maximum adsorption capacities (q_m) decreases with increasing temperature (84.03, 75.19 and 64.10 mg/g at 15, 30 and 45 °C), which indicates that the adsorption is favorable at a lower temperature. Moreover, the high R^2 values (R^2>0.99) of Freundlich isotherm at 30 and 45 °C show a better agreement for the process. The Freundlich isotherm is linear over the entire 14 concentrations at a higher temperature, and the suitable applicability shows that the surface of SD-β-CD is heterogeneous.

SD-β-CD has a good adsorption property and a low cost, so it can be used in the emergency treatment of sudden water pollution. Based on the aniline pollution happened in Zhuozhang River, about 8.7 tons of aniline leaked into the river. The concentration was about 72 mg/L during the early days of the pollution. An absorptive capacity of 16.3 mg/g is used to calculate the amount of adsorbent (The adsorption capacity of SD-β-CD is 16.3 mg/g at 100 mg/L aniline solution (15 °C)). If one tenth of the leaked aniline is removed by SD-β-CD, about 14,092t adsorbent is needed to prepare. The absorption equilibrium can be reached in an hour.

3.2.4 Effect of temperature and thermodynamic parameters

The influence of temperature on adsorption isotherms was discussed under isothermal conditions at 15, 30 and 45 °C, respectively. The adsorption equilibrium versus the temperature at various initial aniline concentrations was calculated (Fig. 7). The influence of temperature on the adsorption equilibrium was not clear for low initial concentrations (<150 mg/L), but the impact became more visible with the increase of initial concentrations (>300 mg/L). The adsorption equilibrium decreases with a rising temperature, which indicates the exothermic nature of the adsorption reaction.

The thermodynamic parameters were considered to determine the energy change in the adsorption process. The standard free energy ($\triangle G^o$), standard entropy ($\triangle H^o$), and standard entropy ($\triangle S^o$) were computed using the following equation:[35,36]

$$\Delta G^o = -RT \ln K \tag{5}$$

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{6}$$

Where K (L/mol) is from Langmuir equation, R (8.314 J/mol K) is the universal gas constant and T (K) is the absolute solution temperature in Kelvin. The $\triangle H^o$ and $\triangle S^o$

values for Eq. (6) are determined by plotting *lnK* against *1/T*. Negative $\triangle G^o$ values were obtained in all three temperatures, which was -14.00, -14.84 and -15.95 kJ/mol at 288.15, 303.15 and 318.15 K, revealing the spontaneous nature of the adsorption. Similar observations were reported for adsorption of cationic dyes onto a cyclodextrin polymer[37] and adsorption of 2,4-didichlorophenol and 2,6-didichlorophenol onto β-cyclodextrin/attapulgite composites.[38] The negative value of $\triangle H^o$ (-4.62 kJ/mol) indicates the exothermic nature of the adsorption interaction, which is consistent with the results of temperature on adsorption equilibrium. And the positive value of $\triangle S^o$ (0.0645 kJ mol^{-1} K^{-1}) shows the affinity of the SD-β-CD for aniline and the increasing randomness at the solid-solution interface.

3.2.5 Adsorption mechanism

The good adsorption ability of SD-β-CD does not originate from the specific surface area, but several interactions act simultaneously on the surface of SD-β-CD. In order to understand the interaction between SD-β-CD and aniline, FTIR were used to test the change of SD-β-CD before and after aniline adsorption. The peaks appeared at 1601 and 1499 cm^{-1}, which were characterized absorption peaks of aniline. As the SD-β-CD does not have a high specific surface area, it is reasonable to assume that the peculiar hydrophobic cavum of β-CD would be the adsorption sites for aniline attachment (Fig. 8). There is 5 g (4.4×10^{-3} mol) β-CD in the reactants, if each β-CD captures one aniline, the maximum possible adsorption capacity will be 82.05 mg/g. From the Langmuir isotherm, the maximum adsorption capacity of SD-β-CD is 84.0, 75.2 and 64.1 mg/g at 15, 30 and 45 °C. From the mechanism of aniline incorporation by CD, the results reveal that SD-β-CD possesses strong adsorption ability for aniline. In fact, the organic film in the surface of sawdust is a kind of gelatin form combination membrane containing β-CD (Fig. 2), which cannot be removed by water or ethanol washing. And the cavity of β-CD is with an internal diameter of 6.5 Å and a depth of 8 Å.[14] Its ability to form inclusion compounds with benzene (6.8 Å) through host-guest interactions explains why SD-β-CD can adsorb aniline. Therefore, SD-β-CD can be used to remove the toxic organic pollutants such as aniline and its derivatives. Besides, SD-β-CD is not a pure substance but a mixture of sawdust, citric acid modified sawdust (CASD) and SD-β-CD. The adsorption of CASD to aniline is more like electrostatic forces, so the benzene peak still appears after aniline trapped by β-CD.

4. Conclusions

In this study, a green adsorbent was successfully synthesized using sawdust, citric acid and β-CD under a mild and green process. The grafting of β-CD onto the sawdust is confirmed by BET, SEM and FTIR analyses. Results show that the SD-β-CD exhibits good adsorption properties towards aniline. The adsorption reaches equilibrium in about 30 minutes, and the optimum pH for the adsorption is at 4-8. The kinetic process follows the pseudo-second order model. Both Langmuir and Freundlich isotherm model can explain the adsorption equilibrium data. The Langmuir model appears to fit the adsorption data better at a lower temperature (15 ℃) and the maximum adsorption capacity is estimated to be 84.03 mg/g

(R^2>0.99). The negative value of standard free energy demonstrates the spontaneous nature of sorption. The proposed adsorption mechanism of SD-β-CD is mainly the inclusion of aniline by β-CD through host-guest interaction.

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Figure Captions

Fig. 1 N_2 adsorption-desorption isotherms of sawdust and SD-β-CD

Fig. 2 SEM images of sawdust, citric acid modified sawdust (CASD) and SD-β-CD

Fig.3 FT-IR spectra of β-CD (a), sawdust (b), citric acid modified sawdust (c), SD-β-CD (d) and the mixture of sawdust, citric acid, and β-CD (e)

Fig. 4 Effect of pH on the adsorption of aniline by SD-β-CD

Fig. 5 (a) Effect of contact time on aniline adsorption by SD-β-CD; (b) pseudo-second-order kinetics for adsorption of aniline (Initial pH 7.0, temperature: 15℃)

Fig. 6 Isotherm plots for aniline adsorption onto SD-β-CD at pH 7.0: (a) Equilibrium isotherms at 15, 30 and 45 ℃; (b) The Langmuir isotherm plots; (c) the Freundlich isotherm plots.

Fig. 7 Effect of temperature on adsorption equilibrium at various initial aniline concentrations.

Fig.8 Schematic diagram of the adsorption process of aniline onto SD-β-CD

Figures

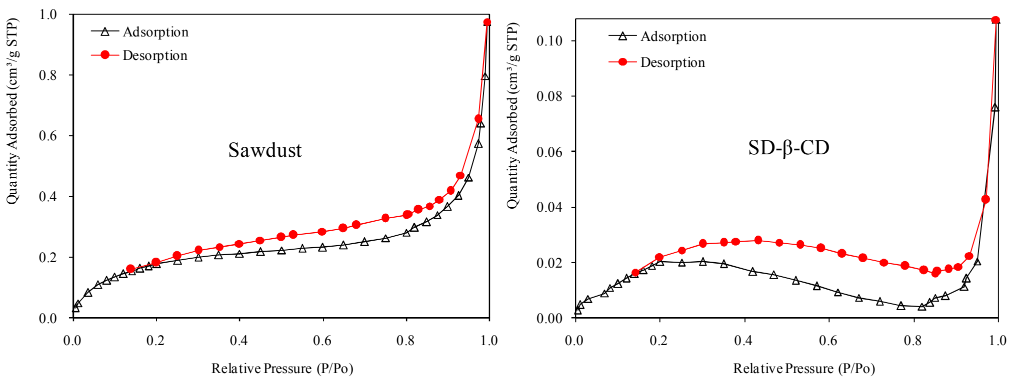
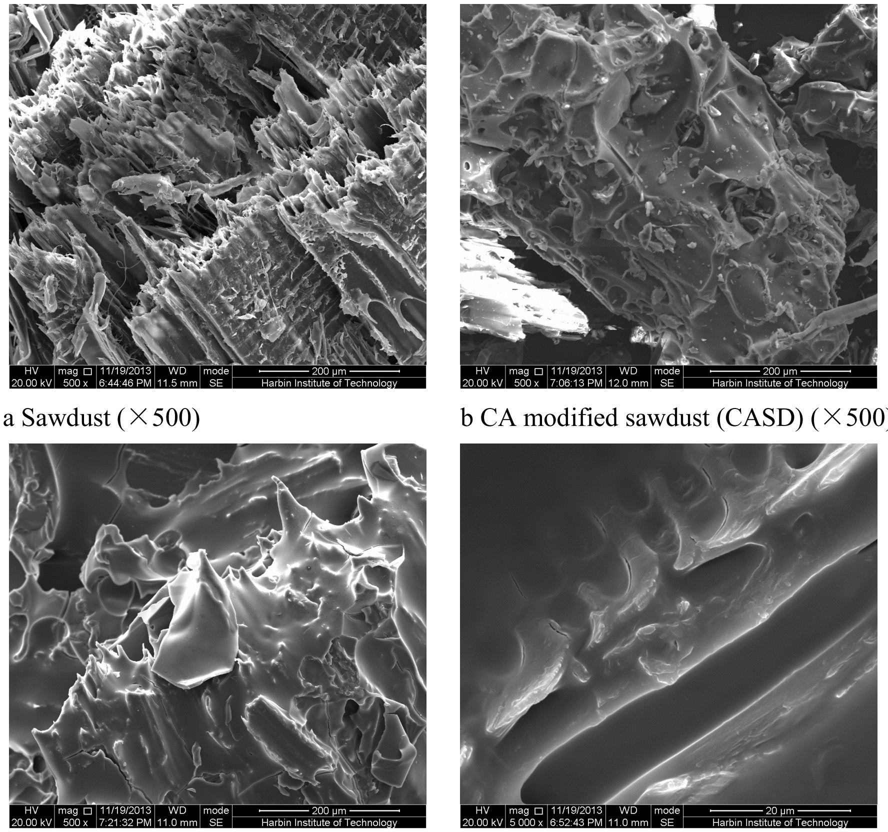


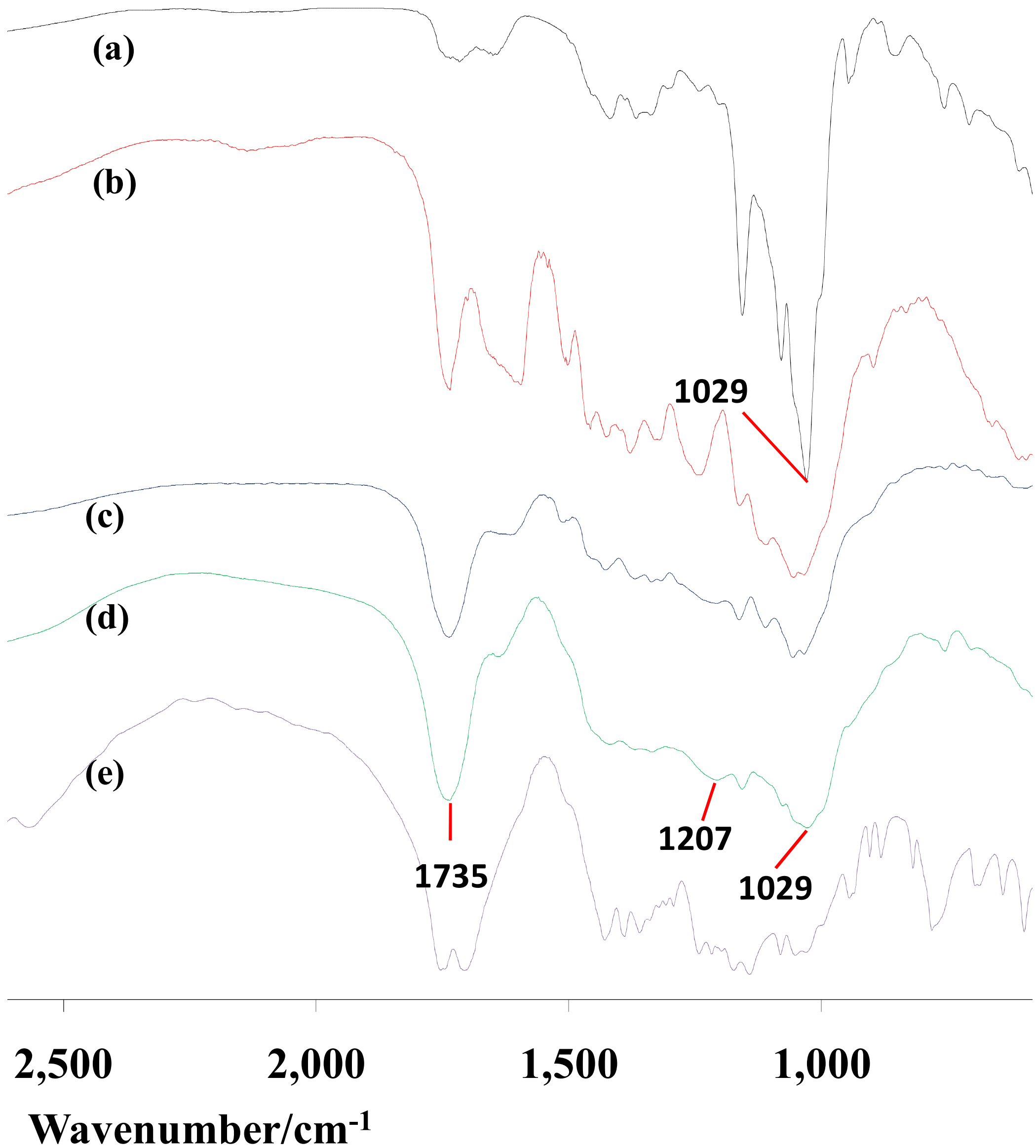
Fig.1. N_2 adsorption-desorption isotherms of sawdust and SD-β-CD



a Sawdust (×500) b CA modified sawdust (CASD) (×500)

c1 SD-β-CD (×500) c2 SD-β-CD (×5000)

Fig.2. SEM images of sawdust, citric acid modified sawdust (CASD) and SD-β-CD



384

385 Fig.3. FT-IR spectra of β-CD (a), sawdust (b), citric acid modified sawdust (c), SD-β-CD (d) and
386 the mixture of sawdust, citric acid, and β-CD (e).

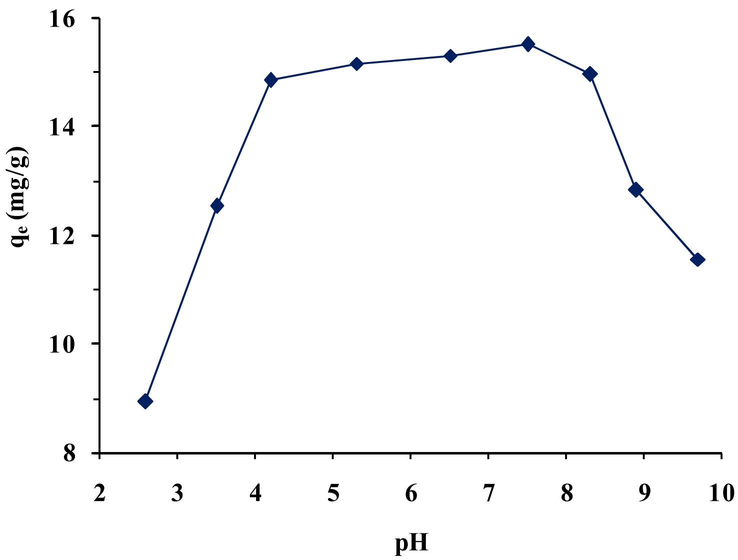


Fig.4. Effect of pH on the adsorption of aniline by SD-β-CD (conditions: adsorbent mass=0.20 g; aniline concentration=100 mg/L; contact time=180 min; agitation speed=135 rpm; temperature=15 ℃).

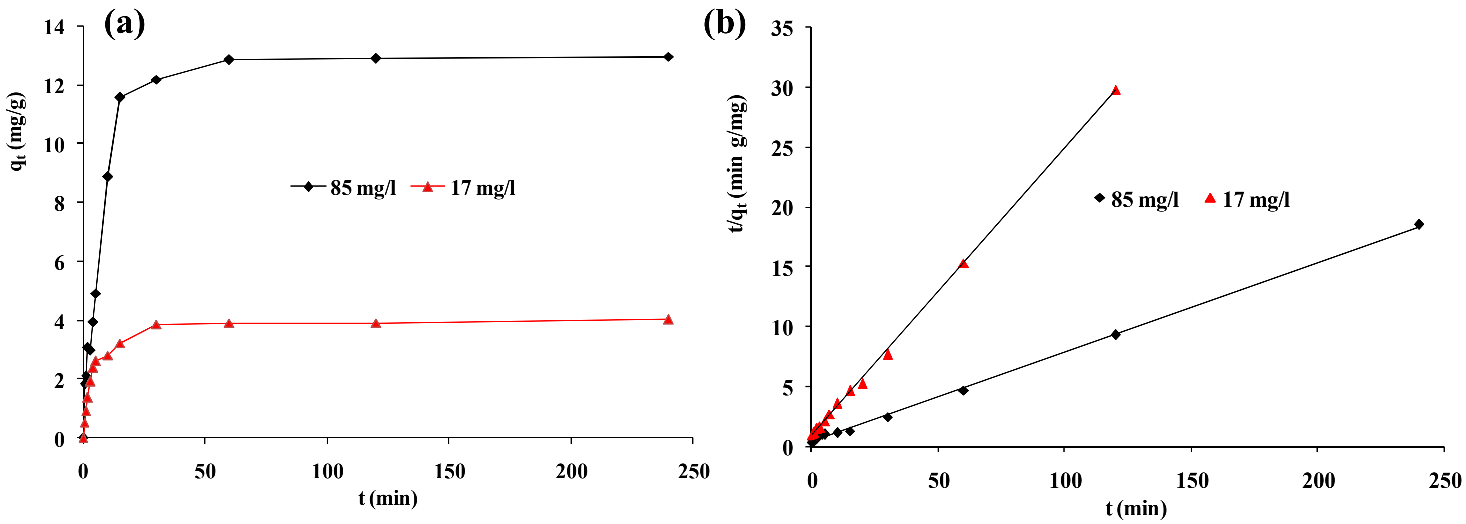


Fig.5. (a) Effect of contact time on aniline adsorption by SD-β-CD; (b) pseudo-second-order kinetics for adsorption of aniline (Initial pH 7, temperature: 15℃)

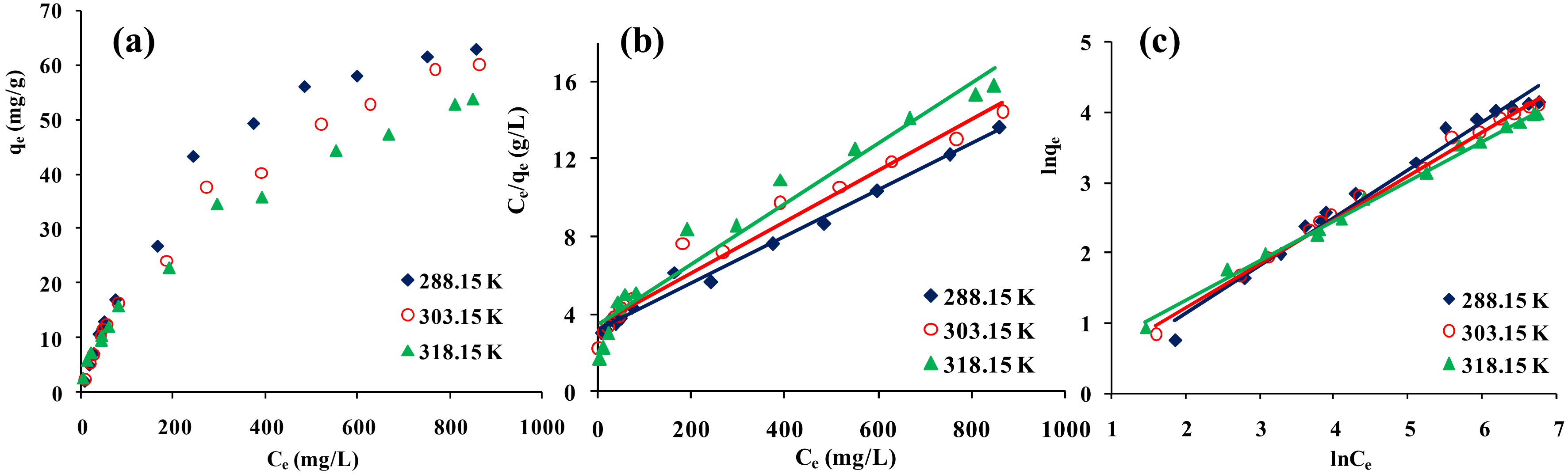
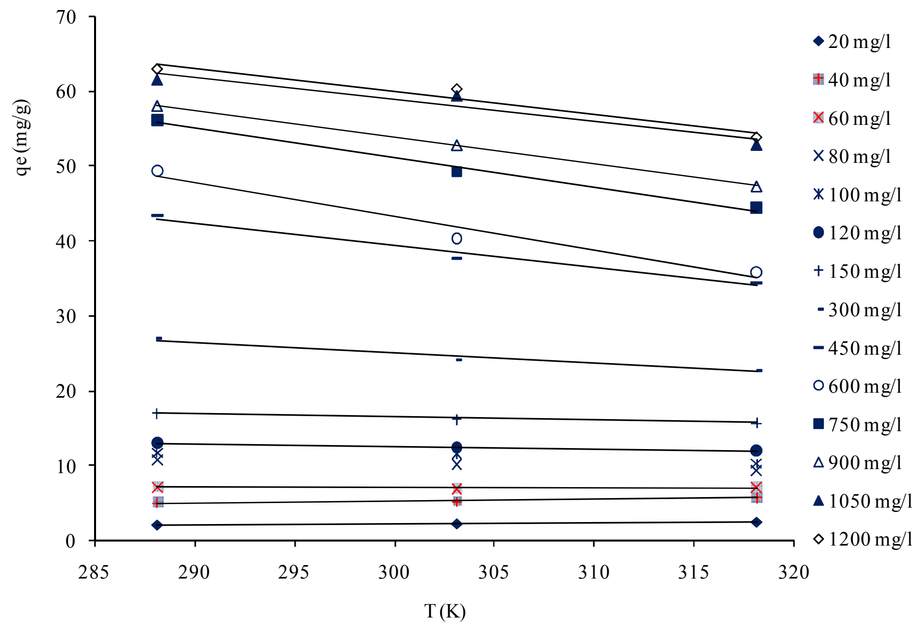


Fig.6. Isotherm plots for aniline adsorption onto SD-β-CD at pH 7: (a) Equilibrium isotherms at 15, 30 and 45 ℃; (b) The Langmuir isotherm plots; (c) the Freundlich isotherm plots.



396
397 Fig.7. Effect of temperature on adsorption equilibrium at various initial aniline concentrations.

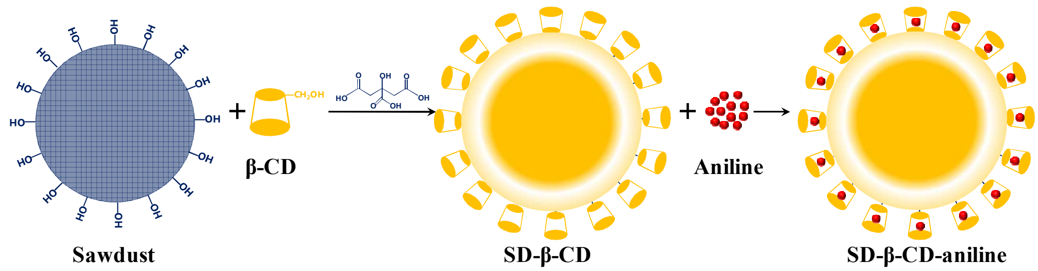


Fig.8. Schematic diagram of the adsorption process of aniline onto SD-β-CD