Chemical Engineering Journal 187 (2012) 69–78

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Study of aniline/ε-caprolactam mixture adsorption from aqueous solution onto granular activated carbon: Kinetics and equilibrium

Bin Tang, Yanwen Lin, Ping Yu, Yunbai Luo*

College of Chemistry and Molecular Sciences, Wuhan University, Wuchang District, Bayi Road, Wuhan 430072, PR China

ARTICLE INFO

Article history:
Received 6 December 2011
Received in revised form 19 January 2012
Accepted 19 January 2012

Keywords:
Aniline
Caprolactam
Granular activated carbon
Adsorption

ABSTRACT

Adsorptive properties of aniline (AN) and ε-caprolactam (CPL) onto a granular activated carbon (GAC) were investigated in single and binary systems via batch adsorption experiments. As AN and CPL are toxic to environment, and they could be present in effluents from CPL manufacturing industries. The effects of pH, GAC dosage, initial adsorbate concentration and temperature on their removal were investigated. The adsorption kinetics of AN and CPL in single and binary systems were studied and was found to conform to pseudo-second order kinetic model. A competitive effect between solutes was observed since lower uptakes as well as slower adsorption kinetics of each solute were obtained in binary adsorption system. The boundary layer diffusion rate was defined as the rate limiting mechanism for AN adsorption on GAC in single and binary system, while the adsorption rate of CPL was found to be governed by particle diffusion. Adsorption isotherm data was fitted to Langmuir and Sips isotherm models for single adsorption system. For the binary solute system, the modified extended Langmuir model was developed to predict the experimental data. The reusability properties of GAC were demonstrated by adsorption–desorption cycle.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

ε-Caprolactam (CPL) is an important chemical raw material which is exclusively used to manufacture Nylon-6 fiber and resins [1]. The global production of CPL amounted to 4.75 million tones in 2011 and there has been an ever increasing demand for it in the recent years. Owing to its high dissolubility in water, CPL could be present in effluents from relevant industries with large quantity. CPL has high COD and toxicity, which may have harmful effect on both public health and environmental quality [2]. Moreover, because of the complexity of chemical reactions required to transform the raw material into CPL, various impurities can be formed during the process of production. Aniline (AN) is one of the main byproducts in the process of CPL production [3]. For this reason effluents from CPL manufacturing industries may contain both CPL and AN. The latter is well known for its wide application in pharmaceutical, pesticide, dyestuff, petrochemicals and agrochemical industries as well as its high toxicity and environmental accumulation. Due to the serious environmental problems created by the pollutants containing wastewater, strict legislation for the release of these hazardous chemicals has been established. Therefore, treatment of pollutants-containing wastewater is required prior to disposal.

Various processes have been employed for the elimination of AN from wastewater, including photodecomposition [4–6], electrolysis [7], extraction [8], adsorption on activated carbon, resin and other adsorbent [9–11], oxidation [12,13], biodegradation [14] and other processes. While techniques available for the treatment of CPL-containing wastewater are limit to extraction [15] and biodegradation [16]. Generally, the technology of adsorption on activated carbon has been recognized as one of the most efficient, promising and widely used techniques in the separation and removal of a wide variety of organic pollutants from wastewater for its relative simplicity of design, operation and scale up, high capacity and low cost. Study of adsorptive removal of AN from aqueous solution has been reported by many researchers [17–20]. However, rather scarce works have been performed to remove CPL via activated carbon adsorption process. Usually, the industrial effluents present a mixture of pollutants, and the interactions of the solutes may be ether cooperative or competitive in the adsorption process. In those multi-component adsorption systems that have been investigated, AN and phenol for instance which have similar adsorption property were often chosen as the target adsorbates, and a synergetic effect between them was reported [19,20]. Competitive adsorption between aniline and other pollutants has been scarce in literature. However, from a practical point of view, the competition between solutes for the active adsorption sites is very

* Corresponding author. Tel.: +86 27 68752511; fax: +86 27 68752511.
E-mail address: ybai@whu.edu.cn (Y. Luo).

1385-8947/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2012.01.088

Table 1
Physico-chemical characteristics of the raw AC.

Parameters	Value
Apparent density (g/mL)	0.65
Ash content (%)	1.22
Moisture content (%)	4.65
pH_{PZC}	6.77
Particle size (mesh)	80–150
BET surface area (m^2/g)	894.73
Micropore volume (cm^3/g)	0.349
Total pore volume (cm^3/g)	0.436
Average pore width (Å)	10.5

common in multi-component adsorption system [21–23], and the selectivity of the sorbent material for the pollutants in the solution is important in the design of adsorption systems. The aim of this work is to investigate the ability of GAC to adsorb AN and CPL from aqueous solution and the selectivity for the pollutants in the solution by the sorbent.

In this work, the adsorption of AN and CPL from single and binary solute system onto a commercial available GAC was investigated. The effects of various operating parameters, such as pH, GAC dosage, initial adsorbate concentration and temperature were studied. The kinetics and isotherms for AN and CPL adsorption onto GAC were studied in single and binary systems. The Webber's intraparticle diffusion and Boyd's film diffusion models were attempted to study the mechanism of adsorption. The kinetic and equilibrium results were obtained from the batch adsorption experiments.

2. Materials and methods

2.1. Materials

2.1.1. Adsorbent

The GAC used in this study was a coal based carbon purchased from Kermel Reagent Co., Ltd. (Tianjin, China). Prior to use, the GAC was washed thoroughly with hot deionized water to remove fines, then dried at 105 °C for overnight and finally stored in a plastic container for further use. The surface properties of the GAC were characterized using a Micromeritics ASAP (Accelerated Surface Area and Porosity) 2020 adsorption apparatus with N_2 as adsorbate at 77 K. The point of zero charge (pH_{PZC}) of GAC was determined by using a mass titration method proposed by Noh and Schwarz [24]. The main characteristics of GAC were given in Table 1.

2.1.2. Adsorbate

AN (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). CPL (purity > 99.9%) was kindly provided by Shijiazhuang Chemical Fiber Plant (SINOPEC, China). They were used as received without further purification and their chemical structures were shown in Fig. 1. The aqueous solutions of the adsorbates for the adsorption test were prepared by dissolving AN and CPL into deionized water without further pH adjustment. For binary solute systems, all solutions were prepared with solution of equal concentrations of AN and CPL.

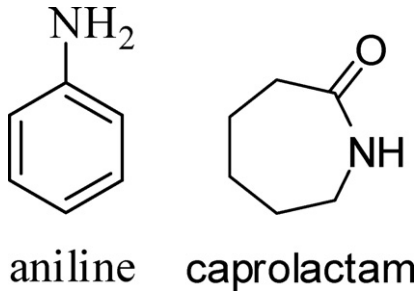

Fig. 1. Chemical structures of aniline (AN) and caprolactam (CPL).

2.2. Batch adsorption experiments

Adsorption of AN and CPL onto GAC from single and binary solute systems was performed in batch experiments. A given mass of GAC was mixed with 100 mL of solution in glass stoppered conical flasks (250 mL). The mixtures were magnetically stirred at 150 rpm and the temperature was kept by thermostated bath. After the specified time, samples were taken from the conical flasks and the adsorbent was separated from the samples by filtering through 0.45 μm microporous filters. The effects of adsorption parameters on adsorption of AN and CPL onto GAC such as pH (3–11), adsorbent dosage (0.5–3.0 g/L), initial adsorbate concentration (0.5–5.0 mmol/L) and temperature (25–55 °C) were investigated. The percentage removal of AN or CPL (%) was calculated according to the following equation:

$$R = \frac{(C_0 - C)}{C_0} \times 100\% \quad (1)$$

The amount of AN or CPL adsorbed onto the GAC, q (mmol/g) was calculated by the following equation:

$$q = \frac{(C_0 - C)V}{W} \quad (2)$$

where C_0 (mmol/L) is the initial concentration of AN or CPL, V (L) is the volume of the solution and W (g) is the weight of GAC and C is the residual concentration of AN or CPL at equilibrium or any time t (min), which defines q_e or q_t, respectively.

In the effect of initial pH studies, the solution pH was adjusted by using 0.1 mol/L NaOH and 0.1 mol/L HCl solutions. The GAC dosage was fixed at 2.0 g/L and the initial concentration of AN or CPL in the solution was 1 mmol/L.

In adsorption isotherm studies, the equilibrium time was set as 24 h according to the result of preliminary experiments. Concentrations of the solutes in the filtrates were determined using HPLC assembled by CBM-10A controller, LC-10AT pumps and SPD-10A dual adsorbance UV detector (Shimadzu, Japan). HPLC was performed using a Shimadzu Shim-pack VP-ODS column (4.6 mm × 150 mm, 4.5 μm) at a flow rate of 0.7 mL/min. The mobile phase used was acetonitrile:water = 30:70 (V/V). The adsorbency wavelength of the UV detector was fixed at 284 nm and 210 nm for the measurement of the concentration of AN and CPL, respectively.

2.3. Adsorbent regeneration experiment

To investigate the reusability of GAC for AN and CPL adsorption, an adsorption–desorption procedure was performed. Firstly, a mass of 0.2 g of GAC was mixed with 100 mL solution and stirred at 25 °C for 2 h. The initial concentration of AN or CPL in the solution was 1 mmol/L. The adsorbed GAC was then immersed in a 20 mL of 0.01 mol/L hydrochloric acid solution and treated with ultrasound for 30 min. The ultrasonic reactor (KSD-3000, Kexingda Co., Ltd., China.) was performed at a frequency of 80 kHz. The regenerated GAC was washed with deionized water to neutral pH and dried at 105 °C for 2 h. The adsorption–desorption procedure was repeated five times.

3. Results and discussion

3.1. Adsorption study of AN and CPL

3.1.1. Effect of pH

The pH of the system plays an important role in the adsorption process for its influence on the surface charge of the adsorbent

Download English Version:

https://daneshyari.com/en/article/150040

Download Persian Version:

https://daneshyari.com/article/150040

Daneshyari.com