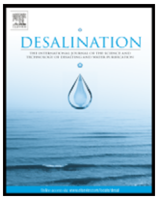
Desalination 257 (2010) 46–52

Contents lists available at ScienceDirect

Desalination

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



Adsorptive retention of citric acid onto activated carbon prepared from *Havea braziliansis* sawdust: Kinetic and isotherm overview

K. Anoop Krishnan [a,c,*], K.G. Sreejalekshmi [b,c], Sumol Varghese [c,d]

[a] Environmental Technology, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Industrial Estate PO, Trivandrum 695019, India
[b] Department of Chemistry, Indian Institute of Space Science and Technology (IIST), Department of Space, ISRO Post, Trivandrum 695022, India
[c] Department of Chemistry, University of Kerala, Kariavattom PO, Trivandrum 695581, India
[d] Department of Chemistry, Mar Ivanios College, Bethany Hills, Nalanchira PO, Trivandrum 695015, India

ARTICLE INFO

Article history:
Received 24 September 2009
Received in revised form 2 March 2010
Accepted 3 March 2010
Available online 27 March 2010

Keywords:
Sawdust activated carbon
Adsorption
Kinetics
Citric acid
Speciation
Isotherm

ABSTRACT

Retention of citric acid, an organic ligand, from aqueous phase was studied using activated carbon (15% K_2CO_3 treated) prepared from *Havea braziliansis* saw dust obtained from a local timber industry at Kodangavila, Trivandrum, Kerala, India. Batch adsorption studies were performed to evaluate the effect of various parameters such as pH, contact time, initial citric acid concentration and adsorbent dose for the adsorptive retention process. The mechanism of citric acid adsorption from aqueous solution was investigated by conducting pH as well as kinetic studies. The maximum adsorption of citric acid onto activated carbon occurred at a pH value around 5.0. The kinetic adsorption data was in close agreement with pseudo-first-order than pseudo-second-order expression. The solution pH, zero point charge (pH_{zpc}) and citric acid speciation played important roles in the extent of citric acid adsorption onto activated carbon from water and wastewaters. The equilibrium data obtained from isotherm studies explains the L-type adsorption process and follows a Langmuir type isotherm model.

1. Introduction

Citric acid is toxic only at higher concentration levels. The adverse effects of citric acid have been noted at concentrations between 0.01 and 5.0 mg/L [1]. The main sources of effluents rich in citric acid are metal plating, metal finishing and metal processing industries. Citric acid (CA) is a poison by intravenous route, moderately toxic by subcutaneous and intraperitoneal route and is mildly toxic by ingestion. It is a severe eye irritant and causes moderate skin, mucous membrane, and upper respiratory tract irritations. It is of low acute toxicity to freshwater fish, daphnia and algae. Moreover, CA is widely used for chemical decontamination process in nuclear reactors [2]. The main pathway through which CA enters the water bodies is from beverage, pharmaceutical, cosmetics, food, chemical as well as detergent industries. Consequently, removal of CA from aqueous solution assumes great concern and is a challenge for researchers who are actively participating in the field of environmental hazardous waste management. As a result, some attempts to remove CA from water and wastewater have been developed in past decades [3–6].

Adsorption was found to be a promising technique for the removal of CA from aqueous solutions and wastewaters [7]. The process of adsorption is an economically viable method and trace amounts of solute can be removed from aqueous solutions. The usage of waste lignocellulosic materials as precursors for the development of adsorbents also makes the adsorption an eco-friendly method for treating effluents. Moreover, application of a waste material for removing another waste material envisages double impact on environmental waste management program. No studies have been reported so far for the removal of CA from aqueous solutions using waste lignocellulosic materials whereas adsorbents derived from lignocellulosic materials have been used for the removal of CA from aqueous solutions [5]. The adsorption capacity of lignocellulosic materials can be increased by chemical/physical means [8]. Carbonization is a good technique for increasing their adsorption capacity for the removal of organic ligands from water and wastewaters [9]. Only a limited number of CA adsorption studies using activated carbon have been reported so far in the literature [5,6]. The adsorption of CA using maghemite [10], pseudoboehmite [7] and clay minerals [3] has also been reported.

In the present study our work mainly focuses on the preparation of steam activated carbon and its application for the adsorption of CA from aqueous solutions. Sawdust from a timber industry was used as a precursor material for the production of activated carbon. The work also aimed to develop adsorption kinetic and equilibrium models for the removal of CA from aqueous phase.

---

* Corresponding author. Present address: Division of Environmental Science, School of Biosciences, University Park, University of Nottingham, Nottingham NG7 2RD, United Kingdom. Tel.: +91 471 2515262; fax: +91 471 2491712.
E-mail addresses: sreeanoop@rediffmail.com, Anoop.krishnan-kutty@nottingham.ac.uk (K.A. Krishnan).

0011-9164/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2010.03.009

2. Experimental procedure

2.1. Preparation of activated carbon

Sawdust of *Havea braziliansis* (rubber wood) collected from local timber industry in Kodangavila, Trivandrum, Kerala, India was used as a precursor material for the preparation of sawdust activated carbon (SDAC). Primarily it was dried under sunlight. The dried biomass was then washed with distilled water to remove surface adhered dirt, filth and water soluble materials and dried at 80 °C for 6 h. About 100 g of dried sawdust was blended with 15% K_2CO_3 solution (chemical activation). The activation process may enhance the pore volume and hence enlarges the diameter of the pores. During activation, the textural properties of adsorbents may change. In chemical activation process, carbonization and activation are carried out in a single step by the thermal decomposition of the precursor material with K_2CO_3. A Matri made (India) furnace was used for the carbonization of sawdust at 600 ± 5 °C. The sample was placed in a purpose-made graphite tube and kept at the middle of the furnace. Steam, produced by a steam generator, entered the graphite tube at a rate of approximately 3 mL/min. The sample was then heated at 10 °C/min to 600 ± 5 °C and held at that temperature for 2 h. After allowing the furnace to cool to room temperature, the carbon was washed with distilled water. The washed product was dried in an air oven at 100 ± 5 °C until constant weight and cooled. The yield of the activated carbon was found to be 37% of that of the original material. The procedure for the preparation of activated carbon was also described in a previous report [9]. The activated carbon particles were sieved to obtain −80 and +230 mesh size (ASTM) particles (average diameter 0.096 mm) using standard test sieves.

2.2. Adsorption experiments

CA obtained from E. Merck (India limited) having 99.0% purity was used for the preparation of ligand solution without any prior purification. A stock solution of CA at 50 mmol/L was prepared in double distilled water and stored at 4 °C in a refrigerator. Experimental solutions of CA having known initial concentrations were prepared by diluting the stock solution. The pH of the experimental solutions was adjusted by adding different concentrations of (0.001, 0.01, 0.1, 1.0 and 2.0 M) HCl or NaOH solutions. About 50 mL of the experimental solutions was mixed with 0.1 g of adsorbent in stoppered conical flasks and the suspensions were equilibrated by shaking (200 rpm) at a fixed temperature using a water bath shaker for a desired period of time. After equilibration, the supernatant liquids were filtered and the concentration of CA was determined using a method described earlier [11]. The amount of adsorbed CA was calculated as

$$q = [(C_o - C_A)V] / m \tag{1}$$

where q, the amount of CA adsorbed onto unit amount of adsorbent (mmol/g); C_o and C_A, initial and equilibrium solution concentration (mmol/L), respectively; V, volume of aqueous phase (mL) and m, mass of the adsorbent (g).

The effect of pH on CA adsorption was studied using initial concentrations of 0.25 and 0.5 mmol/L. The pH of each sample was adjusted between 2.0 and 9.0 as described above. The pH-adjusted solutions were kept at 30 °C for an agitation time of 4 h in a water bath shaker having a constant speed of 200 rpm.

Kinetic studies were performed to evaluate the rate constants for the adsorption of CA from aqueous solution onto SDAC. Equilibrium studies were also conducted using different concentrations of CA (0.25, 0.5, 0.75, 1.0, 2.0 and 3.0 mmol/L) to assess the best fit adsorption isotherm model.

3. Results and discussion

3.1. Adsorbent characterization

The surface properties of SDAC were determined using various instrumental facilities. The surface area of SDAC was determined using the Methylene Blue (MB) adsorption method described by Viladkar et al. [12]. The surface charge density, σ_o, on activated carbon can be determined by potentiometric titration method [13]. Nitrogen adsorption isotherms were determined using Quantasorb surface area analyser (Model QS-7) at 77 K and the data were analysed using Dubinin–Radushkevich (DR) equation [14] for pore volumes, using 0.162 nm^2 for the area of nitrogen molecule and 0.808 g/mL for the density of liquid nitrogen. There are three types of pores commonly seen in solid surfaces namely micro, meso and macro pores. The micropores are the smallest ones having diameter between 0.3 and 2.0 nm and while the size of mesopores is between 2.0 and 50.0 nm in diameter. The macropores are larger in size and having diameter between 50.0 and 10^5 nm. The pH_{zpc} (pH at which the surface charge density becomes zero) of SDAC was obtained from the point of intersection of σ_o against pH curves (Fig. 1). The percentage ash content was determined by the weight difference upon combustion at 750 °C for 4 h. The apparent density, cation-exchange capacity, total acidic sites and carboxylic acid content of SDAC were determined as described in the earlier publication [9]. The surface properties of SDAC are presented in Table 1.

3.2. Effect of pH on CA adsorption

The influence of pH on the adsorption of CA onto SDAC and CAC (commercial activated carbon) was investigated at different pH values ranging from 2.0 to 8.0 (Fig. 2). The amount of CA adsorption on SDAC and CAC increased with increasing pH up to 5.0 and decreased thereafter. That is, below and above the pH 5.0, a decreasing trend in adsorption was observed. Moreover, the maximum removal took place at the pH range 4.0–6.0 for SDAC and only 5.0–5.5 for CAC. At initial concentrations of 0.25 and 0.5 mmol/L, maximum adsorption of 0.113 mmol/g (90.1%) and 0.208 mmol/g (83.3%) was observed for SDAC at pH 5.0. At the same time, maximum adsorption of only 0.092 mmol/g (73.4%) and 0.153 mmol/g (61.2%) was observed for CAC at the same pH.

In order to interpret the adsorption behavior of CA onto carbon surface, knowledge of pH_{zpc} and CA speciation is essential. The surface charge is a function of pH. The pH at which the charge of the solid surface is zero is referred as the zero point of charge (pH_{zpc}). Below pH_{zpc}, the adsorbent surface carries a positive charge and above the surface the charge is negative. Thermodynamic calculations with the

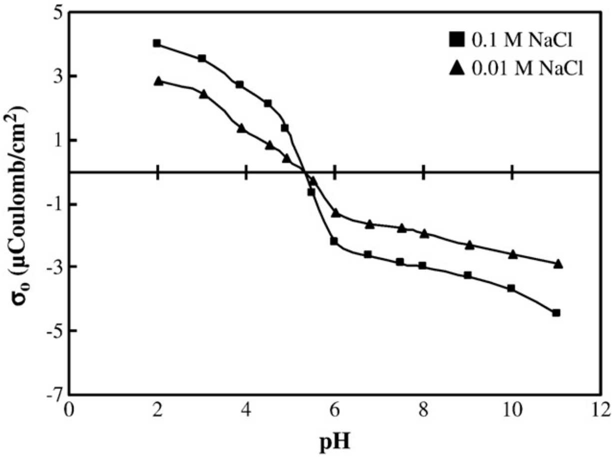


Fig. 1. Effect of pH on the surface charge density of SDAC.