Journal of Water Process Engineering 9 (2016) 233–245

Contents lists available at ScienceDirect

Journal of Water Process Engineering

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

Simultaneous removal of phenol and cyanide from aqueous solution by adsorption onto surface modified activated carbon prepared from coconut shell

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ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form 6 January 2016
Accepted 10 January 2016
Available online 24 January 2016

Keywords:
Phenol
Cyanide
Binary solution
Kinetic
Multi component adsorption isotherm
Thermodynamic

ABSTRACT

The present study is devoted to the elimination of phenol and cyanide from binary component aqueous solution by adsorption onto copper impregnated coconut shell activated carbon (Cu-CSAC). Effects of initial concentration, adsorbent dose, pH, temperature and contact time on phenol and cyanide elimination have been examined. At an optimum temperature 30 °C, pH 8, and the adsorbent dose of 40 g/L, 71.43% phenol and 86.8% cyanide were removed from binary aqueous solution comprising 300 mg/L of phenol and 30 mg/L of cyanide. The isotherm modeling study is carried out by accompanying batch experiments at range of initial concentration 100–1000 mg/L of phenol and 10–100 mg/L of cyanide. Three mono component isotherm model and six binary component isotherm models were considered. The model parameters were predicted by using non-linear regression analysis technique. It was observed that the experimental data indicate a better fit with an Extended Freundlich isotherm model for adsorption of phenol and cyanide in the binary component system. The adsorption efficiency of Cu-CSAC was observed to be 239.85 mg/g of phenol and 5.30 mg/g of cyanide. The mechanism of adsorption process was found chemisorption followed by Pseudo second order kinetics. Thermodynamic studies indicated the adsorption process onto Cu-CSAC as endothermic nature and reversible.

1. Introduction

Currently, environmental pollution by harmful and poisonous compounds is being measured as one of the largest problems in the entire world. Industrial enlargement has improved the discharge of harmful pollutants like phenol, cyanide and their compounds into the atmosphere [1–4]. A huge amount of phenol and cyanide complexes are discharged in effluents from a different industries such as, steel plant, textiles, electroplating, petrochemical, and oil plants [5–8]. Phenol and cyanide are toxic, carcinogenic, and mutagenic. Because of its numerous harmful effects, the elimination of phenol and cyanide from industrial wastewaters earlier their release into water bodies is measured to be essential [9]. These pollutants can cause spiteful taste and odor to the water. The acceptable limit for phenol and cyanide in drinking water according to the US Environmental Protection Agency (USEPA), and the Minimum Nationals Standards (MINAS) of the Central Pollution Control Board (CPCB) in India is 0.5 mg/L and 0.2 mg/L, respectively [2,3].

The conventional treatment methods of phenol and cyanide removal from wastewater such as electrochemical oxidation, chemical coagulation, solvent extraction, membrane separation, and photocatalytic degradation [10–13]. These methods are costly, time consuming and elaborate. Adsorption is very effective and most versatile methods for the elimination of both phenol and cyanide. Wastewater treatment by adsorption of these toxic components using granular activated carbon (GAC) has been widely used by various researchers [14,15]. But due to the high cost and regeneration problem use of GAC is not appropriate for developing countries, therefore, use of GAC moved towards various types of low cost biosorbents [16–18]. Different studies have been made for generating activated carbons from agricultural waste like sugarcane bagasse, nut shells, apricot stones, coconut shell, coconut husk, and tobacco stem [17,19–22]. The high adsorption efficiency of activated carbons is generally correlated to their high-surface-area, porosity and pore volume. The adsorption abilities of activated carbons strongly depend on the nature of source materials.

Coconut shell activated carbon (CSAC) has a very low amount of ash content and also has a micro porous structure. CSAC is

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http://dx.doi.org/10.1016/j.jwpe.2016.01.008
2214-7144/

Nomenclature

Q_t	Uptake of phenol and cyanide at time t (mg/g)
C_t	Liquid phase concentration of phenol and cyanide at time t (h)
C_i	Initial pollutant concentration (mg/L)
C_{eq}	Concentration of adsorbate at equilibrium (mg/L)
V	Volume of the solution (L)
M	Weight of the adsorbent (g)
q_e	Specific uptake of adsorbent at equilibrium (mg/g)
Q_o	Langmuir model constant (mg/g)
b	Langmuir model constant
$Q_{e,i}$	Amount of ith component adsorbed per gram of adsorbent at equilibrium (mg/g)
$Q_{o,i}$	Modified Langmuir model constant for ith component (mg/g)
$C_{e,i}$	Concentration of ith component in the binary mixture at equilibrium (mg/L)
K_F	Freundlich model constant (mg/g)
n	Freundlich model constant
$K_{F,i}$	Extended Freundlich model constant (mg/g)
K_{RP}	R–P model constant (L/g)
a_{RP}	R–P model constant (L/mg)
β	R–P model constant
$\eta_{RP,i}$	Multi component R–P model constant (L/g)
$a_{RP,i}$	Multi component R–P model constant (L/mg)
$\beta_{,j}$	Multi component R–P model constant
x_i, y_i, z_i	Constant in modified R–P model
K_1	Pseudo-first order model constant
K_2	Pseudo-second order model constant
K_{id}	Intra-particle diffusion model constant
ΔG^0	Change in gibbs free energy (kJ/mole)
Δs^0	Change in entropy (kJ/mol K)
Δh^0	Change in enthalpy (kJ/mole)
B_F	Bias factor
NSD	Normalized standard deviation
RMSE	Root mean square error
ARE	Average relative error
MPSD	Marquardt's percent standard deviation
N	Number of observations in the experimental Isotherm
P	Number of parameter in regression model
$Q_{e,i}^{exp}$	Experimental value of Q_e (mg/g)
$Q_{e,i}^{cal}$	Predicted value of Q_e (mg/g)

most widely used as adsorbent for treatment of industrial effluents [23,24]. Surface modification by metal impregnation technique is used for increasing the adsorption capacity of adsorbents. Various authors were using metal impregnation technique in the literature for removal of toxic components due to its high removal efficiency [25–27]. However, very few works have been carried out on the use of copper impregnated CSAC for simultaneous removal of phenol and cyanide.

In the current investigation, adsorption technique in a batch system was employed for simultaneous removal of phenol and cyanide from binary component aqueous solution using Cu-CSAC. The effects of pH, temperature, contact time, dosage, and the initial concentration on removal of phenol and cyanide were examined. Multi component modeling, kinetics and thermodynamic nature of the process were also evaluated.

2. Materials and methods

2.1. Reagents and analytical techniques

All reagents used in this study were AR grade supplied by Himedia Laboratories Pvt. Ltd. Mumbai, India. These compounds were 99% pure. The regulation of the pH is carried out by using AR grade dil HCl and NaOH. Depending on its quantity, phenol and cyanide concentration are analyzed by UV–vis spectrophotometer at wavelengths of 510 and 520 nm respectively [28].

2.2. Preparation and characterization of the surface modified CSAC

Activated carbon was prepared using coconut shell which was taken for the adsorption due to its easy availability and low cost. Coconut shell was collected from local market, IITR, Roorkee, India. The coconut shell was washed with Millipore water several times for dirt removal and then oven dried at 110 °C temperature for 24 h. Thereafter, the sample was crushed and carbonized in a muffle furnace at temp 600 °C for 2 h [29,30]. The acid activation of carbonized coconut shell was carried out by 2 N H_2S0_4 at atmospheric temperature with periodic stirring for about 24 h. The coconut shell activated carbon washed with Millipore water to remove residual chemicals and then the sample was dried at 60 °C temperature for 12 h. The surface modification of CSAC samples was accomplished by conducting a liquid to solid ratio 3:1 of the pretreated activated carbon samples with 300 mL of an aqueous solution of $Cu(NO_3)_2$ in Erlenmeyer flasks over a period of time until complete water was evaporated in an oven at 70 °C [27]. After impregnation, surface area of the adsorbent is found to be decreased. The product obtained by this process was cooled and washed with Millipore water until apparent liquid was acquired. Then adsorbent was dried at 60 °C to be used as copper impregnated coconut shell activated carbon (Cu-CSAC).

The characterization of Cu-CSAC was accompanied by using numerous instruments including Fe-Scanning Electron Microscopy (Fe-SEM) and Fourier Transform Infrared (FTIR) Spectroscopy, Nicolet Avatar 370CsI spectrometer (Thermo Electron Corporation, USA). Physisorption surface analysis on surface area analyzer (ASAP 2010 Micrometrics, USA) was used to calculate surface area (BET) and total pore volume of the biosorbent. UV–vis spectrophotometer was used to identify the concentration of phenol and cyanide from the samples after experiments.

2.3. Experimental procedure of phenol and cyanide removal

The experiments were accomplished in a batch manner with stock solution of phenol and cyanide (1000 mg/L of phenol and 100 mg/L of cyanide), prepared by dissolving accurately weighed quantity of the phenol and cyanide. The solutions of phenol and cyanide were prepared by diluting the stock solution with appropriate volume of Millipore water to obtain desired initial concentration ranging from 100–1000 mg/L of phenol and 10–100 mg/L of cyanide. To study the effects of several operating parameters such as the adsorbent dose, pH, temperature, and initial concentration of adsorbate onto the Cu-CSAC, the batch equilibrium experiments were accomplished. All conical flasks (250 mL) were filled with 100 mL of phenol and cyanide solutions and retained in a temperature controlled orbital shaker at 120 rpm at temp. 30 °C ± 1 for 40 h to attain equilibrium. The pH of the solution was adjusted to between 4 and 12 by adding the appropriate amount of dil HCl and NaOH. The effect of contact time was obtained by varying contact time range 2–40 h. The known amount of Cu-CSAC was added to obtain an adsorbent concentration of 5–60 g/L. All flasks were covered with aluminum foil to avoid contact with light. After