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Simultaneous co-adsorptive removal of phenol and cyanide from binary solution using granular activated carbon

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HIGHLIGHTS

- Optimization of co-adsorption of phenol and cyanide from synthetic coke waste water.
- Multicomponent adsorption isotherms have been applied.
- Kinetic modeling had been performed.
- Thermodynamic parameters of the process have been envisaged.

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ABSTRACT

The present study deals with the equilibrium, kinetic and thermodynamic modeling of simultaneous co-adsorption of phenol and cyanide from binary solution onto Granular Activated Carbon (GAC). The effect of process parameters like pH, temperature, adsorbent dose and contact time on the adsorptive efficiency has been evaluated. At an optimum pH 8, temperature 30 °C and adsorbent dose of 30 g/L, 79.9% of 200 mg/L phenol and 93.6% of 20 mg/L cyanide were removed. Four multicomponent isotherms were applied to the experimental data conducted at an initial concentration range of 100–1000 mg/L. Single component isotherms viz. Langmuir and Freundlich were applied to determine the multicomponent isotherm parameters. It was found that phenol adsorption followed extended Langmuir isotherm while cyanide adsorption followed extended Freundlich isotherm in multicomponent system. The monolayer adsorption capacity of GAC was found to be 269.7 and 1.95 mg/g for phenol and cyanide, respectively as calculated by extended Langmuir isotherm. Adsorption of phenol and cyanide followed pseudo-second order kinetics indicating chemisorption to be the mechanism of adsorption. Thermodynamic parameters viz., ΔG^0, ΔH^0 and ΔS^0 were −3.5174 KJ/mol, −10.326 KJ/mol, −0.0225 KJ/mol-K for phenol and −6.5575 KJ/mol, 14.044 KJ/mol and 0.0679 KJ/mol-K for cyanide adsorption, respectively. Thermodynamic studies established the process of phenol adsorption onto GAC as exothermic and spontaneous in nature while of cyanide as endothermic in nature.

1. Introduction

Remediation of wastewater from coke industries is of prime importance in today's scenario as it contains a number of pollutants in extremely high concentrations (Table 1). Among them phenol and cyanide have been found to be extremely toxic to both human and aquatic life. The MCL (Maximum Contaminant Limit) of phenol and cyanide in industrial discharge has been set as 0.5 mg/L and 0.2 mg/L, respectively by USEPA, WHO and CPCB, India [6]. Exposure to even low concentrations of cyanide can cause coma, heart pains, breathing disorders, thyroid gland enlargement, headaches and even death. On the other hand, phenol exposure can lead to skin and eyes injuries, headache, vomiting, gastrointestinal disorders, central nervous system depression, lung, kidney, liver and heart damage ultimately leading to death [7,8].

In response to increasing health and environmental awareness a number of physical, chemical, biological and combined methods have been employed for removal of phenol and cyanide from industrial wastewater [6,9]. Adsorption of these toxicants has been the most widely accepted method for this purpose and has been applied by many researchers in single solute systems. However, co-adsorptive removal of phenol and cyanide has not been reported yet. Moreover equilibrium isotherms applicable to single solute systems viz. Langmuir, Freundlich, Redlich–Peterson, Toth, Temkin, etc. are not applicable to binary systems in most of the cases. The most probable reason could be the competitive nature

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Nomenclature

BOD	biological oxygen demand (mg/L)
COD	chemical oxygen demand (mg/L)
q	specific uptake capacity of adsorbent(mg/g of adsorbent)
C_0	initial pollutant concentration (mg/L)
C_t	pollutant concentration at time t (mg/L)
V	volume of the solution (L)
M	mass of the adsorbent used (g)
q_e	specific uptake of adsorbent at equilibrium (mg/g of adsorbent)
K_C	equilibrium constant
R	gas constant (J/mol/K)
ΔG^0	change in Gibb's free energy change (kJ/mol)
T	temperature (K)
ΔS^0	change in entropy (KJ/mol-K)
ΔH^0	change in enthalpy (kJ/mol)
MPSD	Marquardt's percent standard deviation
R^2	coefficient of correlation
$q_{e,i}^{exp}$	experimental specific uptake (mg/g)
$q_{e,i}^{cal}$	calculated specific uptake (mg/g)
N	number of observations in the experimental isotherm
p	number of parameters in the regression model
ARE	Average Relative Error
R_L	separation factor
Q_{mix}	adsorption capacity of one adsorbate in mixture
Q_0	adsorption capacity of one adsorbate when present alone
K_f	constant in Freundlich model (mg/g)/(mg/L)$^{1/n}$
n	constant in Freundlich model
$Q_{0,i}$	constant in modified Langmuir model for ith component (mg/g)
$C_{e,i}$	concentration of ith component in the binary mixture at equilibrium (mg/L)
b_i	constant of ith component in Langmuir model (L/mg)
$q_{e,i}$	amount of ith component adsorbed per gram of adsorbent at equilibrium (mg/g)
$K_{F,i}$	constant in extended Freundlich constant for ith component (mg/g)/(mg/L)$^{1/n}$
k_1	rate constant of pseudo-first order kinetic models (h^{-1})
k_2	rate constant of pseudo-second order kinetic model (mg g^{-1} h^{-1})
C_i	intraparticle diffusion coefficient(mg g^{-1})
k_{id}	intraparticle diffusion rate constant (mg g^{-1} h$^{-0.5}$)
x_i, y_i, z_i	constant in extended Freundlich model for ith component

of both the anions and complexity of application of adsorption isotherms owing to competition for the same binding sites as well as solute–surface interactions [10,11]. Thus modified and extended isotherms have been proposed to compensate for inhibition of adsorption of one component by another and vice versa. Multicomponent equilibrium modeling of various metals as well as phenols and its derivatives have been studied extensively [11–13]. But multicomponent modeling of phenol and cyanide adsorption has not been reported till now to the best of our knowledge. For the purpose of adsorption, GAC has been chosen as an adsorbent because of its high adsorption capacity of phenol and cyanide as reported by many researchers [4,14].

The aim of present work is: (i) to determine the optimum process parameters viz., pH, temperature, adsorbent dose and contact time for efficient co-adsorption of phenol and cyanide from binary solution onto Granular Activated Carbon (GAC); (ii) to determine the extent of competition and applicability of multicomponent equilibrium models; (iii) to study the kinetics of the process and (iv) to describe the thermodynamic nature of the process.

2. Materials and methods

2.1. Chemicals and adsorbent

All the chemicals used in this study were of analytical grade and obtained from Himedia Laboratories Pvt. Ltd. Mumbai India. Stock solution containing 100 mg/L cyanide was prepared by dissolving 0.25 g of KCN in 1 L of millipore water (Q-H_2O, Millipore Corp. with resistivity of 18.2 M*X*-cm) whose pH was pre-adjusted to 10 using 1N NaOH. Stock solution containing 1000 mg/L of phenol was prepared by dissolving 1 g of pure phenol crystal in 1 L of millipore water. GAC was washed with millipore water and soaked in 0.5 M H_2SO_4 for 24 h in 2:1 ratio of liquid to solid to increase the surface area and pore volume of GAC. The adsorbent was then washed several times with millipore water and dried in hot air oven at 110 °C for 2 h to completely remove moisture, cooled to room temperature and stored in polybags until further use. The surface area (BET) and total pore volume of the adsorbent was calculated by physisorption surface analysis on surface area analyzer

Table 1
Composition of typical coke wastewater.

Reference/source	pH	Thiocyanates (mg/L)	Thiosulphates (mg/L)	Total nitrogen (mg/L)	Cyanide (mg/L)	Phenol (mg/L)	BOD (mg/L)	COD (mg/L)	Chloride (mg/L)
Prasad and Singh 1989 [1]/Indian Standards 8073	8.5–9.5	50–100	110–220	800–1400	10–50	500–1000	–	–	4000–4200
Ghose et al. 2006 [2]/Jharia coalfield Dhanbad	8.2	–	–	510	10.3	92.82	80.6	692.11	–
Mishra and Bhattacharya [3] 2006	–	–	–	340	80	400	300	700	500
Vazquez et al. 2007 [4]									
Australia	–	184	–	602	93	333	610	2200	
Germany		200–500		350–650	4–15	400–1200	1600–2600	4000–6500	
Spain		215		2255	50	485	1150	3030	
Machon et al. 2007 [5]/Arcelor group steelworks Spain	8.1	363	–	1848	31.8	207	579	1102	1290