Journal of Environmental Chemical Engineering 5 (2017) 526–538

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Adsorption of resorcinol from aqueous solution onto CTAB/NaOH/flyash composites: Equilibrium, kinetics and thermodynamics

Swarnima Agarwal, Ashu Rani*

Department of Pure and Applied Chemistry, University of Kota, Kota 324005, Rajasthan, India

ARTICLE INFO

Article history:
Received 30 August 2016
Received in revised form 3 November 2016
Accepted 25 November 2016
Available online 19 December 2016

Keywords:
Adsorption
Resorcinol
Flyash composite
Surfactant
Kinetic modelling

ABSTRACT

The contamination of water by organic pollutant viz. phenolic compounds is a worldwide environmental problem due to their highly toxic nature. The resorcinol adsorption efficiencies for fly ash (FA), NaOH treated fly ash (NaFA) and surfactant modified NaOH treated fly ash (CTAB/NaOH/flyash composite) were compared. CTAB/NaOH/flyash composite presented higher resorcinol adsorption efficiency than FA and NaFA. This may be attributed to the hydrophobicity imparted by surfactant molecules on the surface of NaFA, consequently leading to organic partioning. The adsorption of resorcinol onto CTAB/NaOH/flyash composite as a function of initial resorcinol concentration, contact time, temperature, ionic strength and solution pH were investigated for their optimization. The adsorbent were characterized by X-ray diffraction (XRD), field emission scanning electro-microscope (FE-SEM), surface area and porosity measurement, Fourier transform infrared (FT-IR) etc. The adsorption kinetics of resorcinol followed a pseudo-second order model. The equilibrium adsorption data were best fitted by Redlich-Peterson isotherm. The resorcinol adsorption capacity slightly decreased with increasing ionic strength adjusted by NaCl. The adsorption was relatively high at solution pH 5.0–6.8 and decreased above pH 7.0. The value of ΔG°, ΔS° and ΔH° indicated spontaneous and endothermic adsorption process.

1. Introduction

Water pollution by organic chemicals is a major problem over decades. Owing to this, there is growing public concern over the contamination of groundwater by organic compounds. The removal of organic contaminants from groundwater or separation of contaminants present in polluted water has become a major focus of research and policy debate. The presence of these compounds even at low concentrations can be an obstacle for reuse of water [1,3]. These organic compounds constitute a very large group of pollutants in the wastewater. Amongst them aromatic compounds especially phenol and its derivatives such as resorcinol, catechol, and cresols are widely found in the effluent of many industries [2,3]. Phenol is present in the surface water of industrial effluents such as coal tar, gasoline, plastic, rubber-proofing, coking, pharmaceutical and steel industries, domestic wastewaters and chemical spillage [4]. Resorcinol is a 1,3-dihydroxybenzene and found in the effluents of many industries such as textile, paper and pulp, steel, petrochemical, petroleum refinery, rubber, dyes, plastics, pharmaceutical, cosmetics etc. [5]. The effluents from synthetic coal fuel conversion process may contain recorcinol and catechol concentrations ranging from 1 to 1000 mg/L [5].

Phenolic compounds are very harmful to organisms even at very low concentration due to their toxicity, foul odour and carcinogenic properties [6,8]. The health effects following repeated exposure to low levels of phenol in water include liver damage, diarrhoea, mouth ulcers, dark urine and hemolyticanemia [7,8]. Resorcinol is classified as a hazardous chemical. Inhalation can cause abdominal pain, nausea, and unconsciousness. It causes redness and pain on skin .It's also considered hazardous to the environment, as it dissolves easily and may infiltrate waterways, presenting hazards to fish and other aquatic life. According to the World Health Organization (WHO), animal studies show that resorcinol caused thyroid dysfunction, effects on the central nervous system, immune system dysfunction and red blood cell change. Ministry of Environment and Forest (MOEF), Govt. of India, New Delhi and United States Environmental Protection Agency (USEPA) has listed phenol and phenolic compound under priority pollutants list. As per the Bureau of Indian Standards, New Delhi,

---

* Corresponding author.
E-mail addresses: swarnima79@rediffmail.com (S. Agarwal), ashu.uok@gmail.com, ashugck@rediffmail.com (A. Rani).

http://dx.doi.org/10.1016/j.jece.2016.11.035
2213-3437/

India, the allowable limit of phenol in drinking water is 1 mg/L while MOEF (Govt. of India) has set a maximum concentration level of 1 mg/L of phenol in the industry effluents for safe discharge into inland surface water and 5 mg/L for safe discharge into public sewers and marine coastal areas [8]. The WHO recommended 0.001 mg/L as the permissible phenolic concentration in portable water. It is therefore necessary to reduce or to eliminate phenols from water and wastewater before discharge or reuse.

Various treatment methods are available for removal of phenolic compounds which include adsorption, ion exchange, reverse osmosis, chemical oxidation, precipitation, distillation, gas stripping, solvent extraction, complexation and even bioremediation [9]. Among them, adsorption is considered to be the cost effective method for quickly lowering the concentrations of phenol and other organic molecule in an effluent. The activated carbon (AC) is widely used for removal of a variety of organics from water, but the generation of carbon fines due to the brittle nature of carbon make it unsuitable in many cases [4]. The challenge is now to find an alternative adsorbent of comparable efficiency with lower cost.Various adsorbents such as mesoporous MCM-41 [1], parthenium based activated carbon [2], granular activated carbon [3], synthetic resin [4], coconut shell [6], agricultural waste material [7], carbonaceous adsorbents [8] andbagasse ash and wood charcoal [9] have been reported for removing resorcinol and phenolic compounds from water and wastewater.

Coal fly ash (FA) is a solid waste generated in large amounts worldwide; therefore, development of new techniques for its productive reuse is important. As a measure to recycle FA, zeolites synthesized from FA (ZFAs) have been extensively investigated in recent years. A number of zeolites have been produced from FA, including Na-P1, philipsite, chabazite, F linde, herchelite, faujasite, analcime, zeolite A, zeolite X, zeolite Y, and hydroxysodalite [10]. It is shown that ZFA is applicable for the removal of a number of pollutants from water, including ammonium [11], heavy metals [12], as well as phosphate [13]. Very encouraging results have also been obtained for ZFA to remove some waste gases from flue [14] because zeolites are hydrated aluminosilicate minerals with a framework formed by tetrahedra of SiO_4 and AlO_4 containing water molecules, alkali and alkaline earth metals in their structural framework [15]. Since zeolites have a net permanent negative charge resulting from isomeric substitution of Si^{4+} by Al^{3+}, cationic surfactants such as hexadecyltrimethylammonium bromide (HTAB) and cetylpyridinium bromide (CPB) are suitable for surface modification of zeolites [15–27]. The positive head groups of cationic surfactants readily exchange with the exchangeable cations on the external surface of zeolites, forming surfactant monolayers [21]. In properly chosen conditions, the loaded cationic surfactants on the external surface of zeolite form bilayers, where the upper layer is bound to the lower layer by the hydrophobic interaction between the tail groups of surfactants in both layers [19]. Surfactant-modified zeolites (SMZs) have been investigated as adsorbents for removing various pollutants such as chromate [16], arsenate [17], phosphate [18], nitrate [19], phenol [20], 4-chlorophenol [20], volatile petroleum hydrocarbons [21], orange II [22], bisphenol A [23], fulvic acid (FA) [24], humic acid (HA) [25] and sodium. However, to our knowledge, the use of SMZs as adsorbents to remove resorcinol from aqueous solution has not been studied.

In the present work a systematic study of the adsorption capacity of resorcinol from aqueous solution by CTAB/NaOH/flyash composite is reported. The effects of several experimental parameters such as contact time, initial adsorbate dosage, initial adsorbent concentration, temperature, ionic strength and solution pH on resorcinol adsorption onto CTAB/NaOH/flyash composite were investigated. The experimental results were analyzed by kinetic and isotherm models. Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated. The mechanism for

Table 1
Chemical composition and properties of coal FA, NaFA & CTAB/NaOH/flyash composite Study.

Parameter	Coal Fly Ash (Wt%) (by XRF)	NaFA(Wt%) (by EDX)	CTAB/NaOH/flyash composite (Wt%) (by EDX)
SiO_2 (%)	60.46	13.74	12.37
Al_2O_3 (%)	21.50	5.99	7.66
Fe_2O_3 (%)	4.30	2.79	4.06
CaO (%)	7.63	2.69	2.42
MgO (%)	0.82	0.23	0.28
Na_2O (%)	0.19	9.42	7.89
K_2O (%)	1.25	0.45	0.24
Moisture (%)	1.2	4.5	5.1
TiO_2	1.53	0.69	0.67
TCEC (mmol g^{-1})	<0.03	1.02	0.815
ECEC (mmol g^{-1})	<0.02	0.068	0.051
Surface area of pores (m^2/g)			
(i) BET	1.7950	18.2875	51.1207
(ii) BJH	1.1465	15.6483	53.1196
a. Adsorption cumulative	1.7148	165528	63.6179
b. Desorption cumulative			
BJH Cumulative Pore Volume (cm^3/g)			
(i) Single Point Total	0.006714[a]	0.102599[b]	0.176996[c]
(ii) BJT Adsorption	0.006264[d]	0.100457[d]	0.169049[d]
(iii) BJH desorption	0.006732[d]	0.102793[d]	0.178586[d]
Average pore diameter (Å)			
(i) Single Point Total	149.6238	224.4138	138.4928
(ii) BJT Adsorption	218.5352	256.7875	127.2969
(iii) BJH desorption	157.0288	248.3996	112.2868

[a] Pores less than 900.1879 Å diameter.
[b] Pores less than 821.9909 Å diameter.
[c] Pores less than 769.8010 Å diameter.
[d] Pores between 17.00 Å and 3000.00 Å diameter.