Evaluation of chitosan-carbon based biocomposite for efficient removal of phenols from aqueous solutions

Usha Soni [a], Jaya Bajpai [a], Sunil Kumar Singh [b], A.K. Bajpai [a],*

[a] Bose Memorial Research Laboratory, Department of Chemistry, Government Autonomous Science College, Jabalpur, MP, India
[b] Department of Chemistry, Guru Ghasidas Central University, Bilaspur, CG, India

ABSTRACT

Nanocomposite particles of chitosan and activated carbon were prepared for removal of phenols from aqueous solutions. The nanoparticles were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) spectroscopy, and particle size and charge analysis. Removal of phenol from aqueous solution was optimized by varying experimental conditions like initial concentration of phenol, pH, adsorbent doses, temperature and contact time. Equilibrium adsorption studies and kinetics of adsorption process showed that adsorption process followed Freundlich isotherm and pseudo-second order kinetic model, respectively. The maximum adsorption capacity of phenol was found to be 409 mg/g.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Contamination of surface and ground waters with aromatic compounds are one of the most serious environmental global problems that have endangered the whole civilization including human beings and living organisms [1]. Owning to its inherent toxicity and good solubility phenols are considered to be one of the potential organic pollutants being discharged into the environment causing severe physiological disorders [2,3]. Major sources of phenol pollutants in the aquatic environments are waste water from the outlets of fine chemical plants such as paints, pesticides, coal conversion, polymeric resins, petroleum and petrochemical industries [4]. Degradation of these substances produces phenols and its derivatives in the environment and its further chlorination as a part of disinfection produces chlorinated phenols which are more toxic and cause other severe hazards. The tolerance limit of the phenol contents in the drinking water is not very high and the concentration should not exceed 0.002 mg/L as per the Indian standard [5]. Phenol is highly toxic and mutagenic substance at large concentration and may be absorbed by the skin. Treatments of this organic compound containing water have drawn significant concern because of the high toxicity of the phenolic compounds.

In recent years, however, many techniques have been applied for purification of phenols contaminated water like ozonolysis, photolysis and photocatalytic decomposition but the success rate is quite low [6]. Traditionally biological treatments, activated carbon adsorption, reverse osmosis, ion exchange and solvent extraction are most widely used techniques for removing phenols and related organic substances [7–10]. However, the adsorption appears to be the most prominent technique for the water reuse in terms of the initial cost, flexibility and simplicity of the design, ease of operation and insensitivity to toxic pollutants [11–16]. It also does not lead to the formation of the harmful substances. Activated carbons are another vital adsorbents and exhibit good adsorption capacity for many organic pollutants [17], but its high cost due to its difficult regeneration and high disposal cost as well as poor adsorption ability to phenols push to explore other adsorbents which could be equally effective but biodegradable so as to reduce the cost of disposal and regeneration. In recent years polymeric adsorbents have found extensive use as an alternative to activated carbons due to their economic viability, adsorbent regeneration properties, presence of large number of functional groups, ease of derivatization into more useful forms, and fairly good mechanical strength.

Chitosan is a kind of positively charged polysaccharide prepared by the N-de acetylation of chitin which makes up the shell and shrimps. Due to the primary, secondary hydroxyl groups and highly reactive amino groups of chitosan as well as the property of the non-toxicity and biodegradability, it has been regarded as one of the preferred materials for separation studies. However, the adsorp-

tion capacity of phenol on chitosan is reported to be low [18]. and some studies on chemical modification of chitosan have also been carried out to enhance its activity through addition of novel ligand into its structure [19]. Many industrial applications of chitosan are known due to the secondary amino groups of chitosan which show poly-cationic, chelating and film forming properties along with high solubility in the dilute acids.

2. Experimental

2.1. Materials

Chitosan, activated carbon, acetic acid, toluene, tripolyphosphate (TPP) and phenol used were of analytical reagent grade and supplied by Merck India. Water used for preparation of solutions was generated in the laboratory by double distilling the deionized water in a distillation unit. The stock solution of phenol was prepared by dissolving 100 mg phenol in one litter water. All other required reagents were of analytical grade quality.

2.2. Preparation of the adsorbent

Chitosan based biosorbent was prepared by emulsion crosslinking method. In brief, for preparation of adsorbent a known amount of chitosan was dissolved in 10 mL of 1% acetic acid solution and after its homogenous mixing a requisite amount of activated carbon was added in it. The whole mixture was stirred on a magnetic stirrer for about 1 h at room temperature while for preparing w/o emulsion, 10 mL paraffin-oil was added in to homogenous mixture of chitosan-charcoal suspension. The above solutions were mixed on a magnetic stirrer for 2 h to form a stable emulsion. Now to this stable emulsion 10 mL of TPP solution of 0.1 M concentration was dropwise added and stirred for 4 h at room temperature. The nanocomposite particles so prepared were cleaned by washing frequently with toluene and acetone. The final particles were dried at room temperature and stored in an air tight polyethylene bag.

2.3. Characterization

Prior to using the prepared adsorbent for adsorption experiments, the adsorbent was characterized by the following techniques.

2.3.1. Fourier transforms infrared (FTIR) spectroscopy
The FTIR spectra of prepared chitosan based biosorbent were recorded on a FTIR-8400, Shimadzu spectrophotometer. Samples for the spectral analysis were prepared by mixing adsorbent and KBr in 1:10 proportion and the spectra were obtained in the range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1}.

2.3.2. SEM/EDX analysis
A scanning electron microscope inter-phased with an electron dispersive X-ray spectrometer (SEM/EDX, JEO, JSM-5800LV) was used to study the surface morphologies and elemental analysis of chitosan based nanocomposite and activated charcoal.

2.3.3. X-Ray diffraction (XRD) analysis
In order to ascertain crystalline nature of the chitosan based nanocomposite. XRD analysis were performed on a rotating X-ray diffractometer in the 2θ range of 10–70 °C.

2.3.4. Particle size and particle charge analysis
The sample was prepared by dispersing a definite amount of nanoparticles in ethylene glycol, having a viscosity 0.0100 cP as the dispersant. The dispersant was placed in the disposable zeta cell and the surface charge of the nanocomposite was determined

using Zetasizer Nano (Backman Coulter Delso Nano C.) Dynamic light scattering technique was used to determine particle size. The zeta potential distribution was determined from the zeta potential (Mv) versus intensity (kcps) curve and the measurements were performed at 25 °C with the count rate of 2272.3 kcps.

2.4. Quantification of phenol solution

The concentration of phenol in aqueous solution was determined by measuring absorbance at wavelength of 269 nm, using a UV spectrometer (model Shimadzu UV-1500). In order to reduce measurement errors in all the experiments, the UV adsorption intensity of each solution sample was measured in triplicate and the average value was used to calculate the equilibrium concentration based on standard calibration curve, whose correlation coefficient (R^2) was found to be 0.9872.

2.5. Adsorption studies (Batch process)

Adsorption experiments were carried out using the batch contact method. In brief, 50 mg of chitosan based nanocomposite was added into a 10 mL of phenol solution at constant pH and temperature. The suspension was shaken on a thermostat shaker (Rivotech India) for 1 h to attain equilibrium at the room temperature (30 °C). After shaking was over the mixture was filtered through the Whatman filter paper (2.5 size particle retention). The adsorption capacity of the adsorbent was determined by material balance of the initial and equilibrium concentrations of the solution.

The adsorbed amount and the percentage removal of phenol were calculated by using the following equations, respectively.

$$\text{Absorbed amount } (\text{mg/g}) = \frac{C_i - C_f}{m} \times V \quad (1)$$

$$\% \text{ removal} = \frac{C_i - C_f}{C_i} \quad (2)$$

Where C_i is the initial and the C_f the final concentrations of the metal ion solutions (mg/L),

V is the volume of the adsorbate solution, and m being is the weight of adsorbent (chitosan composite). The pH of the solution was adjusted using required volumes of 0.1 M HCL and/or 0.1 N NaOH before adding the adsorbent.

2.6. Statistical analysis

All measurements were done at least 3 times and graphs have been plotted along with the respective error bars.

3. Results and discussion

3.1. Fourier transform infrared (FTIR) studies

FTIR spectra of chitosan, chitosan-carbon nanocomposite particles, before and after adsorption are shown in Fig. 1(b–c), respectively. The FTIR spectrum of chitosan(1-a) shows a broad and strong band at 3431 cm^{-1} is due to overlapping of the OH and N—H stretching vibration of functional groups engaged in hydrogen bond [20]. The band at 2910 cm^{-1} and 2874 cm^{-1} is due to symmetric and asymmetric − CH$_2$ vibration attributed to pyranose ring. A peak at 1653 cm.$^{-1}$ is C═O stretching in amide group band,1572 cm^{-1} is N—H bending in non acetylated 2-amino glucose primary amine, The sharp peak at 1381 cm^{-1} is C—N stretching. The peaks at 1068 cm^{-1},1035 cm^{-1},are skeletal vibration involving the CO stretching which are characteristic of chitosan saccharide structure and 663 cm^{-1} is due to −NH$_2$ wagging vibration peak.

The following changes were observed in the FTIR spectra of chitosan based nanoparticles after adsorption (Fig. 1b), the absorption