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Removal of ciprofloxacin hydrochloride from aqueous solution using vertical bed and sequential bed columns

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ABSTRACT

In the present paper column studies for the removal of ciprofloxacin hydrochloride from aqueous solution using vertical and sequential bed adsorption columns using ZnO nanoparticles and groundnut shell powder (GSP) as adsorbents have been discussed. Bed depth service time model (BDST) has been used to determine the column parameters i.e length of the column, bed depth and flow rate. Studies at varying drug concentrations and flow rates have been carried out at pH 4 for ZnO nanoparticles and 6 for groundnut shell powder i.e the pH where maximum adsorption of ciprofloxacin has been found to occur in batch studies using ZnO nanoparticles and groundnut shell powder. The bed capacity for ZnO nanoparticles has been found to be 6.1 mg/g and 6.24 mg/g using a vertical bed and sequential bed column respectively and for groundnut shell powder it is 5.59 mg/g and 6.29 mg/g for a feed concentration of 80 mg/L and flow rate 5 ml/min. at 298 K temperature. Analyses of breakthrough curves show that the time taken by columns for 50% breakthrough and 90% exhaustion increases with increase in the feed concentration and flow rate. The Thomas model and Yoon-Nelson models are in good agreement with experimental data. It is found that the bed capacity for sequential column, which is easier to handle and use, is slightly better than that of vertical column and can be considered for use in small scale industries.

1. Introduction

Pharmaceuticals are a major source of water pollution due to inappropriate disposal in the water bodies by the pharmaceutical industries, inappropriate disposal of sewage sludge in soil and human excretion [1,2]. Of the various classes of drugs, antibiotics specifically the fluoroquinolones are major component. They are introduced into aquatic environment vie disposal of untreated/inappropriately treated waste water and gets accumulated through food chain [3,4]. Drugs consumed by human body are not completely metabolised after digestion thus human excretion contains both metabolised and non metabolised forms of drugs [5]. Ciprofloxacin hydrochloride (1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid) is a broad-spectrum antibiotic belonging to fluoroquinolone family is widely used as human and veterinary medicine [6,7]. Small amount of fluoroquinolones have been detected in the wastewater effluent in United States in the concentration range of 0.6-2 μg/Land in Switzerland, the amount of ciprofloxacin hydrochloride in domestic sewage was found to be in the range of 249–405 ng/L [8]. Though the detected amount is very minute but due to its high toxicity to human, animal and aquatic lives it is not desirable even at very low concentration [2,8]. Ciprofloxacin hydrochloride can cause health problems like headache, diarrhea, tremors, nausea, vomiting, etc [9,10]. It is, therefore important to remove this contaminant from waste water. Investigations related to removal of fluoroquinolones from water using various adsorbents in batch mode have been reported in recent years [2,11,12] but only sporadic reports are available pertaining to the performance of the adsorbents using continuous flow adsorption columns [4]. Results of batch adsorption experiments are not sufficient for designing a water treatment system on industrial scale for continuous operation and laboratory scale continuous flow column studies are necessary for this purpose [13,14]. In recent years with the advancement in nanotechnology, nanoparticles are considered as efficient adsorbents for the removal of pharmaceutical pollutants from wastewater due to their tiny particle size and larger availability of surface sites [15–17]. However, agricultural based adsorbents are also gaining a lot of importance because they are inexpensive, freely available in bulk, have good adsorption potential and there is no need of regeneration [6,10]. With a view to consider the comparative efficiency of the different classes of adsorbents, as well as to ascertain the capability of these adsorbents for industrial applications, in the present work continuous flow column studies using vertical bed as well as

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sequential bed columns have been carried out for the adsorption of ciprofloxacin hydrochloride on ZnO nanoparticles and groundnut shell powder as adsorbents. The use of sequential bed column has been relatively little studied [18], though it is more easily manageable, can be dismantled and handled with ease and there is a lesser possibility of clogging of adsorbent bed and no mechanical device is required [18].

2. Material and methods

2.1. Preparation of adsorbent

2.1.1. Preparation of ZnO nanoparticles

Zinc oxide nanoparticles have been prepared using precipitation method [19], 25 ml of 4.0 M NaOH (Merck) solution was added dropwise into 25 ml of 0.2 M $ZnSO_4$ (Merck) solution with continuous stirring under atmospheric conditions. The final pH of the mixture was fixed at 13 and the temperature of the mixture maintained at 60 °C. The obtained precipitates were washed and dried in an air oven. The purity of ZnO nanoparticles has been ascertained by X-ray Diffractometer (Powder Method, Panalytical.s X.Pert Pro), UV (UV–vis 2450 spectrophotometer, Shimadzu, Japan), BET (Quantachrome NovaWin version 11.04), FTIR (Model RZX Perkin Elmer), SEM (Model JSM6100 Jeol with image analyzer) and TEM (Hitachi, H-7500).

2.1.2. Preparation of groundnut (Arachis Hypogaea) shell powder

Groundnuts were purchased from local market and deseeded. The shells were washed with water and dried in sun light for 2–3 days. The shells were finely ground and after sieve analysis particles of 250–420 micron size were used as adsorbent [20]. The characterisation has been done by proximate analysis, XRD, BET, FTIR and SEM techniques

2.2. Preparation of adsorbate solution

Stock solution of ciprofloxacin hydrochloride having drug concentration 100 mg/L was prepared by taking 33.3 ml of the opthalmic ciprofloxacin hydrochloride ($C_{17}H_{18}FN_3O_3{\cdot}HCl{\cdot}H_2O$, molecular wt. 385.82) with purity 99.8% (Cipla Ltd. Pharma Zone, Phase II, Indore Special Economic Zone, Pithampur (M.P), INDIA) and made upto 1000 ml with double distilled water [21]. Further dilutions were carried out with double distilled water to obtain the concentration desired for study (i.e 80 mg/L, 90 mg/L and 100 mg/L). Ciprofloxacin is freely soluble in water and sparingly soluble in methanol and ethanol [7,21]

2.3. Estimation of ciprofloxacin

Estimation of the drug has been carried out using reported method [21]. Drug solution of concentration 100 mg/L was diluted to prepare the working standard solutions of concentration range 1 mg/L to 10 mg/L, as the absorbance value was found to be greater than 1 beyond this concentration range. To determine the amount adsorbed in experimental solutions of concentration 80 mg/L, 90 mg/L and 100 mg/L, samples of drug before and after adsorption were diluted with fixed amount of water accordingly to get the concentration within the calibration range of 1–10 mg/L. Thereafter calculations to get the actual concentrations were done after applying the dilution factor. U.V- visible spectrophotometer, (Shimadzu 2450, Japan) with 1 cm optical path length quartz cells was used for all absorbance measurements [21]. At different pH, ciprofloxacin exists as different species, therefore λ_{max} varies with change in solution pH and separate calibration curves were plotted, for the estimation of ciprofloxacin, for each pH studied with the respective λ_{max} using water as blank. Column adsorption experiments have been carried out at pH 4 for ZnO nanoparticles and 6 for groundnut shell powder. At these pH values, wavelength for maximum absorbance of ciprofloxacin hydrochloride was found to be 275 nm (Fig. 1).

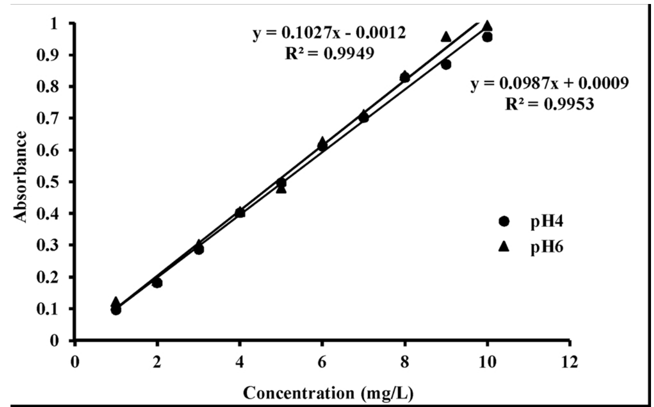

Fig. 1. Standard calibration curves for ciprofloxacin hydrochloride at pH 4 and 6.

2.4. Column adsorption studies

With a view to study the effect of adsorbate concentration, continuous flow column studies have been carried out for the removal of ciprofloxacin hydrochloride by varying feed concentrations (i.e 80 mg/L, 90 mg/L and 100 mg/L) at the influent flow rate of 5 ml/min., 7.5 ml/min. and 10 ml/min. using both vertical and sequential bed adsorption columns [18,22]. The pH of the solution is maintained at 4 for ZnO nanoparticles and at 6 for groundnut shell powder. These values of the pH are those at which maximum removal of ciprofloxacin hydrochloride occurs using batch studies [21]. The flow rate of adsorbate solution was controlled using rotameter for both columns. After adsorption, samples have been collected at regular time intervals from bottom end of the column until the column become saturated (i.e C_t = $0.9C_o$). Drug concentrations have been determined spectrophotometrically using U.V–vis spectrophotometer, (Shimadzu 2450, Japan) at the wavelength of maximum absorbance i.e 275 nm.

2.5. Experimental setup

2.5.1. Vertical column

A vertical column of 1.5 cm diameter and 20 cm height containing adsorbent was set up (Fig. 2). The adsorbent is packed up to a depth of 4 cm (obtained from Bed Depth Service Time (BDST) model); (5.2 gm ZnO nanoparticles and 4 gm groundnut shell powder).The down flow mode was used and the flow through the column was maintained using a rotameter [18,23]. Samples from the bottom end of the column are withdrawn at regular intervals of time, for estimation of drug.

2.5.2. Sequential bed column

The sequential bed column was setup by connecting four bent glass tubes in a manner shown in Fig. 2 to contain adsorbent in each tube. The setup is so adjusted as to facilitate the free flow of adsorbate solution under gravity [18]. The amount of adsorbent taken in each tube is 1.3 gm for ZnO nanoparticles and 1gm for groundnut shell powder. The first tube, filled with solid adsorbent, received the influent which flowed through the second tube and so on. Samples have been collected from the end of the column, at regular intervals of time, to determine the drug concentration.

2.6. Breakthrough curves

To evaluate the performance of continuous flow adsorption column, a study of breakthrough curves is desirable. The breakthrough curve is expressed as the plot of C_t/C_o against time of contact (t), where C_t/C_o is ratio of effluent concentration (C_t) to the adsorbate inlet concentration (C_o). For the present study the breakthrough point is taken as the point