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Removal of bromophenols from water using industrial wastes as low cost adsorbents

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Abstract

A comparative study of the adsorbents prepared from several industrial wastes for the removal of 2-bromophenol, 4-bromophenol and 2,4-dibromophenol has been carried out. The results show that maximum adsorption on carbonaceous adsorbent prepared from fertilizer industry waste has been found to be 40.7, 170.4 and 190.2 mg g^{-1} for 4-bromophenol 2-bromophenol and 2,4-dibromophenol, respectively. As compared to carbonaceous adsorbent, the other three adsorbents (viz., blast furnace sludge, dust, and slag) adsorb bromophenols to a much smaller extent. This has been attributed to the carbonaceous adsorbent having a larger porosity and consequently higher surface area. The adsorption of bromophenols on this adsorbent has been studied as a function of contact time, concentration and temperature. The adsorption has been found to be endothermic, and the data conform to the Langmuir equation. The further analysis of data indicates that adsorption is a first order process. A comparative study of adsorption results with those obtained on standard activated charcoal sample shows that prepared carbonaceous adsorbent is about 45% as efficient as standard activated charcoal in removing bromophenols. To test the practical utility of this adsorbent, column operations were also carried out. The results were found satisfactory in removing bromophenols by column operations. Therefore, the present investigations recommend the use of carbon slurry waste as inexpensive adsorbent for small scale industries of developing/poor countries where disposal of solid waste of various industries and proper treatment of polluted wastewater is a serious problem.

Keywords: Bromophenols; Pollutants; Industrial wastes; Adsorbents; Batch and column studies

1. Introduction

Among the various aqueous pollutants generally present in wastewaters, phenol and substituted phenols are considered as priority pollutants [1]. The discharge of effluents containing phenolic pollutants from various industries into natural water bodies is an ongoing and serious threat to human health and natural water quality. The ubiquitous nature of phenols, their toxicity even in trace amounts and the stricter environmental regulations make it necessary to develop processes for the removal of phenols from wastewaters. Various methods for the removal of phenols from wastewaters include coagulation, chemical oxidation, solvent extraction, liquid membrane permeation and adsorption [2]. Among these, adsorption onto activated carbon proved to be one of the efficient and reliable physiochemical treatment methodology in wastewater treatment. In spite of the usefulness of activated carbon as an efficient adsorbent for wastewater treatment, the high cost of activated carbon inhibits its large scale use as adsorbent. Hence, an economical and easily available adsorbent would certainly make an adsorption based process a viable alternative for the treatment of wastewater containing phenolic pollutants. In recent past, considerable attention has been devoted to develop the low cost adsorbents from various materials, but the utilization of agricultural [3,4] and industrial wastes [5,6] is increasingly becoming of vital concern because these wastes represent unused resources and, in many cases, cause serious disposal problems. If these wastes could be used as low cost adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low cost adsorbent if developed can reduce the pollution of wastewaters at a reasonably cost.

We have carried out recently the comparative studies of adsorbents prepared from the industrial wastes of fertilizer and steel plants [7,8] and have found that carbonaceous adsorbent

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(prepared from fertilizer industry waste) having high organic content adsorbs organic molecules efficiently. In order to further test the applicability of this adsorbent, investigations have been further extended to a number of bromophenols, viz., 2-bromophenol, 4-bromophenol and 2,4-dibromophenol. Further, the results have also been compared with those obtained on standard activated charcoal and adsorbents of inorganic nature prepared from steel industry wastes. The present communication reports these results.

2. Experimental

2-Bromophenol (2-BP), 4-bromophenol (4-BP) and 2,4-dibromophenol (2,4-DBP) were procured from Lancaster (England), Spectrochem (India) and Fluka (Switzerland), respectively. The standard activated charcoal sample was obtained from E. Merck. Other reagents used were of AR grade. Double distilled water was used for preparing solutions throughout these investigations.

2.1. Preparation of carbonaceous adsorbent

The carbon slurry waste material was procured from National Fertilizer Ltd. (NFL), Panipat (India) and powdered. It was found to consist of small, black and greasy granules and treated [7,9] with H_2O_2 to oxidize the adhering organic material. It was then washed with distilled water and heated at 200 °C till the evolution of black soot stopped. The activation of this material was done at different temperatures in muffle furnace for 1 h in the presence of air. After the activation, the ash content was removed by treating the material with 1 M HCl and washed with distilled water and dried. The surface area of samples activated at temperatures 300, 400, 500, 600 and 700 °C were found to be 280, 363, 380, 374 and 367 $m^2 g^{-1}$, respectively. Thus, the activation at 500 °C imparts maximum surface area and it was also seen that extent of adsorption was maximum for this sample activated at 500 °C. Therefore, all studies reported in this paper are on a sample activated at 500 °C. The yield of the finished product was found to be ∼90% and it is now called 'carbonaceous adsorbent'. Different mesh sizes were obtained after sieving and kept in desiccator for further use.

2.2. Preparation of blast furnace sludge, dust and slag adsorbents

These adsorbents were prepared from wastes obtained from Malvika Steels, Jagdishpur (India) by the method reported elsewhere [7]. The products were sieved and stored in desiccator.

2.3. Instrumentation

The spectrophotometric determination of bromophenols was done on Shimadzu 1601 UV–vis spectrophotometer (detection limits were 0.25 mg L^{-1}). The pH of solutions was measured with ELICO LI 127 pH meter. Vario EL III, CHNS Elemental Analyzer was used to determine the carbon content of the adsorbents and LEO 435 VP was used for scanning electron microscopy (SEM). IR spectra of the samples were recorded on a Perkins-Elmer FTIR spectrophotometer model 1600. X-ray measurements were done on a Phillips X-ray diffractometer employing Cu Kα radiations.

2.4. Adsorption studies

2.4.1. Batch studies

The adsorption of bromophenols on prepared adsorbents was studied at room temperature (25 ± 2 °C) by employing the batch method. Known volume (10 mL) of bromophenols solution of varying initial concentrations, taken in 50 mL glass tubes, was shaken with a fixed dose of adsorbent (0.01 g) for a specified period of contact time in a thermostated shaking assembly. The glass tubes were tightly stoppered (covered) to avoid vaporization losses of bromophenol from the aqueous solutions. After equilibrium, the concentration of the adsorbate in the residual solution was determined spectrophotometrically at λ_{max} of 274.0 nm for 2-bromophenol, 280.0 nm for 4-bromophenol and 286.0 nm for 2,4-dibromophenol, respectively. The reproducibility during concentration measurements was ensured by repeating the experiments at least three times under same conditions and average values are reported. Standard deviations were found to be within ±5.0%. Furthermore, the error bars for the figures were smaller than the symbols used to plot the graphs and hence are not shown.

The amount of bromophenols adsorbed (q in mg g^{-1}) was determined as follows

$$q = (C_0 - C_f)\frac{V}{m} \quad (1)$$

where C_0 and C_f are the initial and final concentrations of the adsorbate in solution (mg L^{-1}), V the volume of solution (L) and m is the mass of the adsorbent (g).

The pH of the solutions was adjusted using 0.1N HCl and 0.1N NaOH solutions. pH of the solutions was measured before and after the equilibration and a slight change in pH was observed. The initial pH value of all bromophenols solutions was from 5.8 to 6.8 before experiments. After the experiments, the pH value was observed from 5.5 to 6.5 for all the bromophenols. However, after adjustment of the pH of adsorbent–adsorbate system, no further change was observed. The adsorption was studied as a function of contact time, initial concentration and temperature.

2.4.2. Column studies

In the present investigations, a glass column (50 cm × 1.05 cm) was fully loaded with adsorbent on a glass–wool support. Double distilled water was used to rinse the adsorbent and to remove any bubbles present. A bromophenol solution or wastewater containing mixtures of phenols and other materials was poured over the column and the column effluent was allowed at a flow rate of 2.5 mL min^{-1}. A definite amount of the column effluent (10 mL) was taken and the concentration of the solute (pollutants under investigation) determined from time to time by spectrophotometric method. This process has continued until the concentration in the column effluent started