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Removal of Organic Pollutants by the Use of Iron(III) Hydroxide-Loaded Marble

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ABSTRACT

Iron(III) hydroxide-loaded marble (Fe-marble) was studied as an adsorbent to remove phenolic compounds from aqueous solution. The coordination of ligands with the central metal ion occurs through the phenolic oxygen. Sorption and breakthrough capacities were determined. The effects of pH and concentration were studied. Adsorption remains unaffected in the 2–6 pH range. Fe-marble exhibits good sorption capacities for phenolic compounds, and the adsorption data follow the Langmuir model as well as the Freundlich model. Some experiments were also performed with a view to recovery phenols and create *in-situ* regeneration of spent adsorbent column. The phenols adsorbed were quantitatively eluted with 1 M NaOH solution. The column can be used for 4–5 cycles consecutively.

INTRODUCTION

Most phenols are toxic (1, 2), and many are known or suspected human carcinogens (3, 4). Very small concentrations of phenols cause a disagreeable odor, particularly when waters containing phenols are chlorinated (5) for disinfection. Serious difficulties have been caused at waterworks in many parts of the world by the discharge into raw water of industrial effluents from gasworks, wood distillation, oil refineries, chemical plants, etc. (6). Accordingly, a water-treatment process is necessary to reduce phenol content below the regulation value.

The most common methods for the removal of phenols from aqueous solutions are solvent extraction (7, 8) and chemical oxidation (9, 10). Such treatments result in the formation of hazardous by-products (11).

Other phenol-removal methods, e.g., adsorption on activated carbon (12, 13), anion-exchange resins (14, 15), iron diethanolamine (16), zinc silicate in the Fe(III) form (17), and chelating resin in the Fe(III) form (18), have been discussed. However, despite their usefulness, these methods have several drawbacks such as disposal of enormous volume of sludge and high cost of treatment.

In the present work a rapid and effective method for phenol adsorption is developed by use of iron(III) hydroxide-loaded marble. This phenol-removal method is of great advantage over other methods with respect to both solid/liquid separation and cost.

EXPERIMENTAL

Preparation of the Adsorbent, Iron(III) Hydroxide-Loaded Marble

The white marble was ground and sieved to 60–100 mesh. Then the marble particles were rinsed with distilled water several times and dried in an electric oven (100°C).

The resultant marble particles (50 g) were soaked in an aqueous solution containing 2% w/v iron(III) chloride (200 mL) for 24 hours. Then the iron(III) hydroxide-loaded marble particles (dark brown) were well rinsed with distilled water, dried (100°C), and sieved on 120 mesh to remove the free hydroxide particle resulting from the preparation of Fe-marble.

Determination of Iron Loaded on Fe-Marble

The Fe-marble (1.00 g) was completely dissolved in 10 mL hydrochloric acid (12 M). The iron in the solution was determined spectrophotometrically with 1,10-phenanthroline (19).

Phenol Adsorption Procedure

Phenolic compounds were dissolved in double-distilled water or ethanol, depending upon their solubility. The 4-amino-antipyriene procedure (20) was used for the spectrophotometric determination of pyrocatechol, pyrogallol, quinol, resorcinol, phenol, and 2-chlorophenol. Nitrophenols were directly estimated spectrophotometrically at 360 nm.

Adsorption experiments were performed by shaking 20 mL adsorbate (0.1 g/L, pH $\approx$ 6) solutions and a definite amount of adsorbent (0.2 g) in a stoppered glass flask for 6 hours at 30°C. The biological degradation of phenols was also taken into account by running blank determinations.

Kinetic Measurement

The kinetics of phenol adsorption on Fe-marble was observed by using a batch technique. A number of stoppered Pyrex glass flasks containing a given volume (20 mL each) of solutions of phenol (0.1 g/L, pH $\approx$ 6) and 0.2 g Fe-marble were mechanically agitated at predetermined time intervals, separated from the adsorbent material, and analyzed to determine the uptake of phenol.

Breakthrough Capacity

The breakthrough behavior of different phenols was studied by passing phenolic solutions (1 mg/10 mL, pH $\approx$ 6) through a glass column (0.40 cm i.d.) loaded with 2 g Fe-marble. The flow rate was maintained at ~0.5 $mL \cdot min^{-1}$.

RESULTS AND DISCUSSION

The results of iron(III) leakage studies in various solvents revealed that iron(III) hydroxide deposition on a marble surface is strong except in acidic solutions (pH < 1).

The results of adsorption studies presented in Table 1 reveal that adsorption capacity varies from 1.47×10^{-2} to 8.63×10^{-2} mmol/g for different phenols. The adsorption capacity of Fe-marble for phenols is determined by their ability to form complexes of varying stability with iron(III).

The adsorption mechanism of iron(III) hydroxide on marble may be as follows. When white marble (a pure variety of calcium carbonate in which the crystals are wedged compactly together) is soaked in iron(III) chloride

TABLE 1
Adsorption of Phenols on Iron(III) Hydroxide-Loaded Marble

No.	Phenol	Adsorption capacity $\times 10^2$ (mmol/g)
1	Pyrogallol	7.65
2	Pyrocatechol	8.63
3	Resorcinol	4.18
4	Quinol	5.72
5	Phenol	3.56
6	2-Chlorophenol	1.94
7	*p*-Nitrophenol	2.26
8	2,4-Dinitrophenol	1.47

solution, the following reaction occurs on the marble surface:

$$2Fe^{3+} + 3CaCO_3(\text{marble}) + 3H_2O \rightarrow 2Fe(OH)_3 \downarrow + 3Ca^{2+} + 3CO_2 \uparrow$$

The strongly acidic aquo-iron(III) complex immediately reacts with the calcium carbonate of the marble and generates colloidal iron(III) hydroxide with the evolution of carbon dioxide gas. The generated iron(III) hydroxide colloid is effectively and tightly deposited onto the marble surface.

The nature of phenol adsorption onto iron(III) hydroxide surface may be elucidated on the basis of the ligand-exchange reaction (21) of hexacoordinate iron(III) on the Fe-marble surface (H_2O or OH ligand $\rightarrow$ phenol)

$$ROH + [Fe(H_2O)_6]^{3+} \rightleftharpoons H_2O + [Fe(H_2O)_5(ROH)]^{3+}$$

$$[Fe(H_2O)_5(ROH)]^{3+} + H_2O \rightleftharpoons H_3O^+ + [Fe(H_2O)_5(RO)]^{2+}$$

The kinetic measurements plotted in Fig. 1 reveal that equilibrium is attained within 90 minutes on a Fe-marble adsorbent.

Figures 2 and 3 show the adsorption of pyrocatechol on Fe-marble as a function of pyrocatechol concentration in aqueous solution. These adsorption isotherms are linear. Thus, the adsorption mode is of a typical

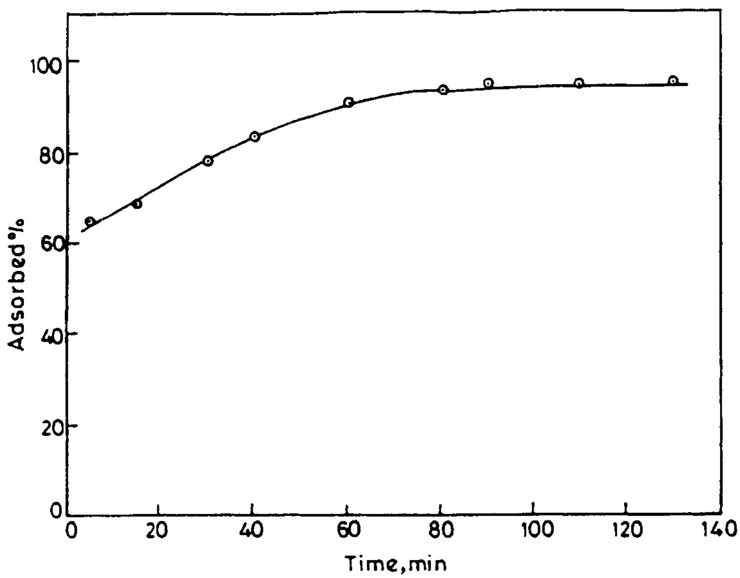

FIG. 1 Rate of uptake of pyrocatechol.

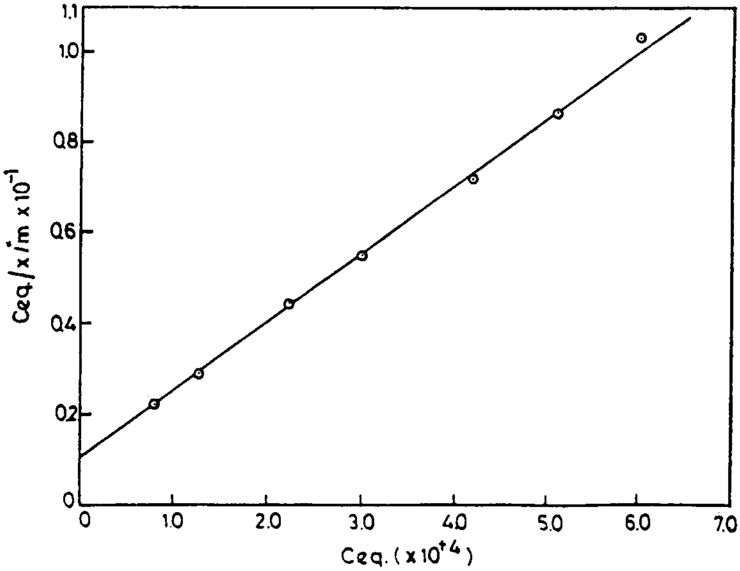

FIG. 2 Plot of Langmuir adsorption isotherm for pyrocatechol.

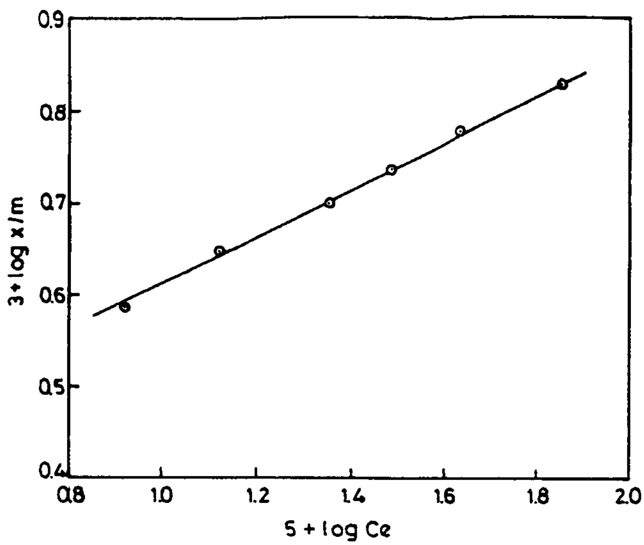

FIG. 3 Plot of Freundlich adsorption isotherm for pyrocatechol. Amount of adsorbent: 0.2 g/20 mL.

Langmuir (22) as well as Freundlich (23) isothermal nature. The Fe-marble exhibited much higher adsorptivity compared to unloaded marble.

The effect of pH on the percent removal of phenolic compounds by Fe-marble (Fig. 4) indicated that their removal is almost unaffected in the 2–6 pH range. Removal was considerably decreased when the pH of the initial solution was above 6. This may be due to the competing hydroxide ions.

The breakthrough curves of phenols are plotted in Fig. 5. The results reveal that 6 bed volumes of phenol, 9 bed volumes of resorcinol, 12 bed volumes of quinol, 18 bed volumes of pyrocatechol, and 20 bed volumes of pyrogallol, corresponding to a retention of 6, 9, 12, 18, and 20 mg, respectively, can be passed through a column of Fe-marble without any trace being detected in the effluent. On unloaded marble, breakthrough was obtained in the first bed volume for all phenols.

Removal of adsorbate and regeneration of a column is an important process in wastewater treatment. To achieve this and in order to assess the practical utility of the adsorbent, studies were undertaken on column operations. A glass column, 40 × 0.4 cm, was filled with 2 g Fe-marble. The column was loaded with phenolic compound and the solution was percolated downward at a flow rate of 0.5 mL/min. Almost complete desorption of phenolic compounds could be achieved with 1 N NaOH solu-

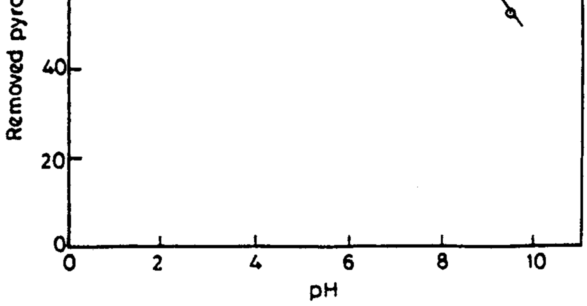

FIG. 4 Effect of pH. The aqueous phase initially contained 2 mg pyrocatechol. The pH was adjusted by use of 0.1 M hydrochloric acid and 0.1 M sodium hydroxide solution.

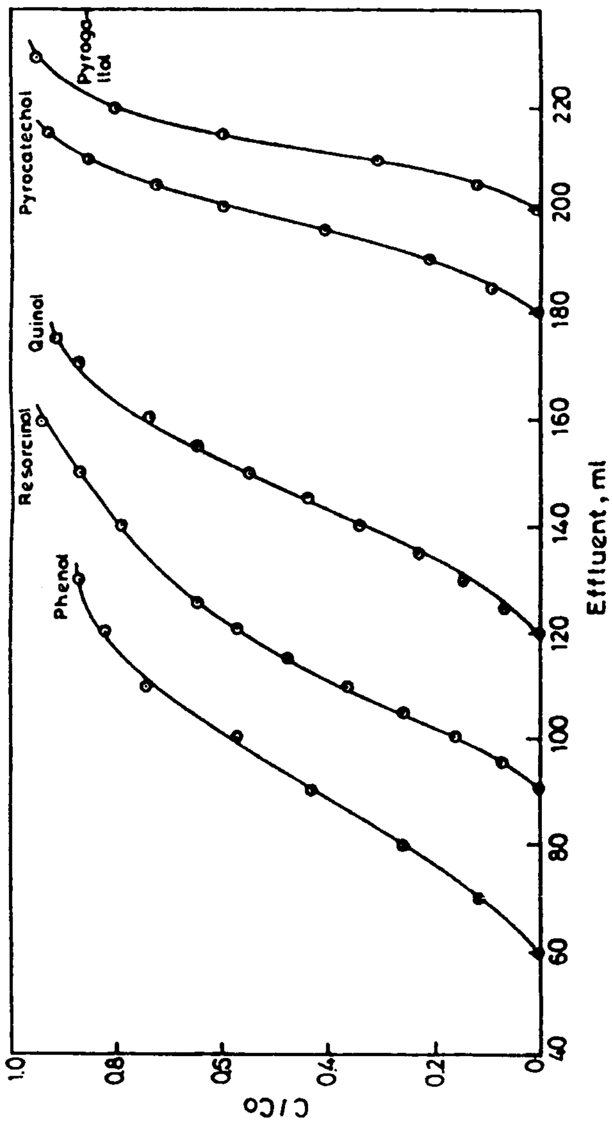

FIG. 5 Breakthrough curves of phenols on column operation. C_0 and C denote the initial concentration and the concentration in each effluent fraction, respectively.

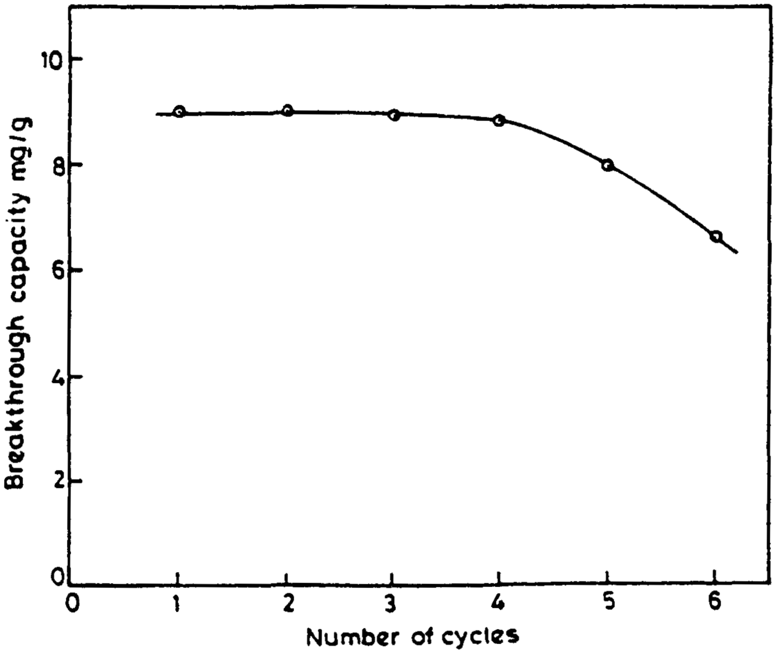

FIG. 6 Breakthrough capacity for pyrocatechol as a function of the number of cycles.

tion. This is probably due to the ligand-exchange reaction (phenol → H_2O or OH), and thus the sodium salts of phenolic compounds were easily eluted.

The column was washed with distilled water until the washings were neutral and then treated with 10^{-3} M HCl (10 mL). The data of cyclic capacity plotted in Fig. 6 show that the column can be used for 4 cycles with almost no loss in capacity.

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