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Adsorption of Pyridine by Acid Treated Spent Bleaching Earth

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The adsorption of pyridine on acid treated spent bleaching earth was studied as a function of time, pH and initial concentration. Lagergren first order rate equation was used to describe the adsorption rate of pyridine and adsorption rate constants were calculated. Rate constants of intraparticle diffusion were also calculated. Adsorption isotherms were modelled by the Langmuir equation and the constants of this isotherm were calculated. The dependence of the adsorption of pyridine on the pH of the solution was studied to find the optimum pH value. In order to study the effect of pH on the adsorption of pyridine, experiments were carried out at different pHs. The maximum adsorption was found to occur at pH 6.5. Giles isotherm was used and adsorption type was determined.

Key Words: Spent bleaching earth, Pyridine, Picolines, Adsorption.

INTRODUCTION

Pyridine is widely used as a solvent and intermediate in the production of piperidine, agricultural chemicals, drugs, dyestuffs, paints, rubber products, polycarbonate resins and textile water-repellents[1,2]. It is introduced into natural ecosystems as a result of the production of these substances. Many of pyridine derivative compounds are hazardous in nature and persist for a longer duration in the environment as they are poor substances to indigeneous microorganisms[1,2]. Therefore, the removal of pyridine derivatives from a water stream is of great importance.

A variety of methods have been used for removal of pyridine and its derivatives from water and waste water. The most commonly methods include adsorption[1-8], biodegradation[9-12], ion exchange[3], ozonation[13] and electrochemical oxidation[14]. Among these processes, adsorption processes produce good quality effluents and are very effective processes to remove pyridine and its derivatives. Activated carbons are the most common adsorbents for the removal of organic pollutants and inorganic pollutants since they have high surface area and porosity. However, activated carbon has some disadvantages since its price and regeneration cost are high. Therefore, low cost alternatives are being continuously investigated.

In recent years, attention of scientists have been devoted to the study of different types of low cost materials such as adsorbents produced from spent bleaching earth[15-18], agro-industry waste[19], tree fern[20], orange peel[21], montmrollonite[22], chitosan[23], egg shell[24], coal mining waste[25-27], coffee residue[28], brick powder[29], perlite[30], used tires[31,32] and biogas slurry[33].

In this study, spent bleaching earth (SBE) which is a solid waste from edible oil processing industry was chosen as a starting material to produce a new adsorbent. SBE has two components: residual oil not removed by filter pressing and montmorillonite clay. This material is disposed of directly to landfill option either dry or as a wet slury. But the landfill option causes problems, the most dangerous being pyrogenic nature of unsaturated oil which rapidly oxidizes on clay surface to the point of spontaneous ignition.

The constant changes in environmental legislation has led to restrictions in solid waste management. Therefore, it is necessary to study on the minimization of pollutant such as SBE from oil industry and a good solution from an environmental and economic standpoint is the application in the waste water industries as a low cost adsorbent. Therefore, in this study SBE was chosen as raw material to produce a new adsorbent. The aim of this study is to investigate the adsorption capacity and adsorption kinetics for removal of pyridine from aqueous solutions by the adsorbent produced from SBE.

EXPERIMENTAL

All chemicals used in the study were analytical grade. A stock solution of 250 mg L^{-1} was prepared from pyridine. All solutions were prepared with double distilled water. All the other chemicals used in the study were obtained from Merck.

Preparation of the adsorbent[16]: Impregnation with acid (H_2SO_4) was performed by mixing 24 mL acid solution (8 mL water + 16 mL H_2SO_4 96 %) with 25 g spent bleaching earth (SBE) into a paste which has been carbonized in a static air muffle furnace in covered crucibles at 350 ºC for 5 h. Post treatment was carried out with 0.1 M HCl solutions, hot and cold water, then acetone and finally impregnated samples were dried for 16 h at 105 ºC. The surface areas of the fresh activated bentonite and the adsorbent produced from SBE were measured by nitrogen adsorption method and found to be 207 and 198 m^2 g^{-1}, respectively. The carbon and hydrogen contents were measured to be 21.52 and 3.17 % for SBE and 7.49 and 0.56 % for the adsorbent produced from SBE. Similar results were reported by Pollard *et al.*[34].

The results of pore structure measurements for both the fresh activated bentonite and the adsorbent produced from SBE are presented in Table-1. It is seen from the comparision of the activated bentonite and adsorbent produced from SBE that there is not significiantly change in the volume of pores. It is also seen from the results for 0-5 mm pore diameter that there is no change in the values of volume of pore for both materials. This can be explained by the fact that large molecules in the oil can not access these narrow pores. Therefore, some of the pores are not covered with organic layer.

Treatment process removed the much of the substances existing in the pores of spent bleaching earth. This was supported by elemental analysis results for SBE and adsorbent produced from spent bleaching earth.

TABLE-1
PORE DISTRIBUTION FOR FRESH BENTONITE AND
ADSORBENT PRODUCED FROM SPENT BLEACHING EARTH (SBE)

Pore diameter (nm)	Fresh bentonite volume of pores ($cm^3 g^{-1}$)	Adsorbent produced from SBE volume of pores ($cm^3 g^{-1}$)
0-5	0.010	0.010
0-14	0.271	0.258
0-25	0.303	0.281
0-80	0.343	0.329

Batch experiments: Batch adsorption experiments were carried out using acid treated spent bleaching earth with pyridine solutions of different glass bottles in a thermostated shaker. All the experiments were carried out at 20 ºC. At the predetermined time intervals, samples in glass bottles were centrifuged at 6500 rpm and the concentration of supernatant was determined using a spectrophotometer. The pH of the solutions were adjusted by 0.1 M HCl and NaOH.

RESULTS AND DISCUSSION

Effect of pH on the adsorption of pyridine: The pH of the aqueous solution is an important variable which controls the adsorption at the water-adsorbent interfaces. Therefore, the adsorption of pyridine on acid treated spent bleaching earth was examined at different pH values ranging from 2.7 to 9.1 and presented in Fig. 1. It is seen from Fig. 1 that pyridine removal increases with increasing pH and the removal of pyridine is maximum at pH = 6.5. There is also no significantly change in the adsorption of pyridine between pH 6.5 and 9.1. Similar results were also obtained in some studies[1,2]. Therefore all the other experiments were carried out at pH = 6.5.

The chemical interaction of pyridine derivatives with activated carbons can be shown by the following equilibria as given by Weber[6] and further utilized by others[3,8,35-38]. The M^+ represents the exchangeable cations on the adsorbents while H^+ refers to the hydronium ions. Py represents the pyridine or pyridine derivatives.

$$Py + H^+ \rightleftharpoons PyH^+ \tag{a}$$

$$Py + AC \rightleftharpoons Py\text{-}AC \tag{b}$$

$$PyH^+ + M^+ - AC \rightleftharpoons PyH^+ - AC + M^+ \tag{c}$$

$$H^+ + PyH^+ - AC \rightleftharpoons H^+ - AC + PyH^+ \tag{d}$$

$$H^+ + AC \rightleftharpoons H^+ - AC \tag{e}$$

$$Py - H^+ - AC \rightleftharpoons PyH^+ - AC \tag{f}$$

In the low pH region [pH ≤ (pK_a = 5.2)], pyridine is mostly converted to protonated pyridine (PyH^+) *via* reaction eqn. (a) and the adsorbent has the positively charged surface[1,2]. The strong electrostatic repulsive forces push the particles of pyridine from the surface of the adsorbent. Therefore, the repulsion between the positively charged pyridine and the adsorbent surface decreases the adsorption. In the higher pH region [pH ≥ (pK_a = 5.2)], pyridine is converted to unprotonated pyridine and the adsorption forces between the adsorbent and pyridine are mainly dispersion forces and these forces result in the higher adsorption[39,40]. These results suggest that the dominant sorption mechanism is given by eqn. (b). Other reactions given by eqn.(a), (c)-(f) play insignificant role in the adsorption mechanisms of pyridine onto spent bleaching earth.

Effect of time on the adsorption of pyridine: Fig. 2 shows that the variation of pyridine concentration with time. Equilibrium time is 120 and 200 min for the initial concentrations of 20 and 35 mg L^{-1} and depends on the initial concentrations.

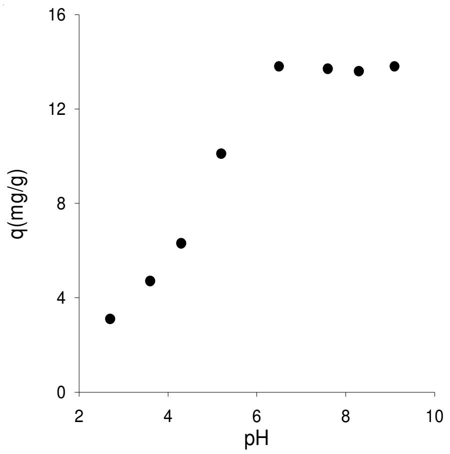

Fig. 1. Effect of pH on the adsorption of pyridine

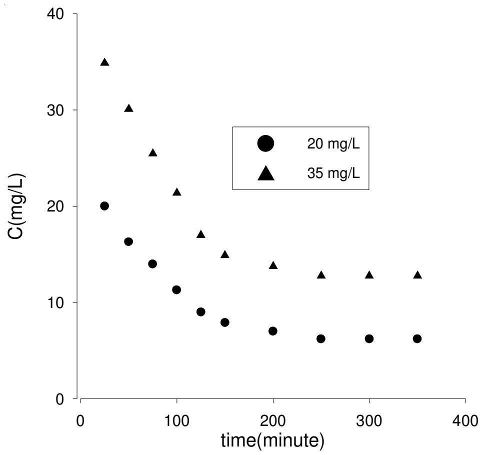

Fig. 2. Variation of concentration with time

Adsorption kinetics: The Lagergren first order rate equation was applied to the determination of adsorption rate constant of pyridine. The Lagergren equation can be written:

$$\ln(q_e - q) = \ln q_e - k_a t$$

where q and q_e are the amounts of pyridine adsorbed at time t and equilibrium respectively, k is the rate constant. The linear plots of ln (q_e - q) *versus* time show the applicability of this equation and the values of k were calculated from the slope of straight lines and found to be 0.021 and 0.020 min^{-1} for the initial concentrations of 20 and 35 mg L^{-1} (Fig. 3).

Intraparticle diffusion: In adsorption studies, it is necessary to determine the rate-controlling step. Therefore, the results obtained from the experiments were used to study the rate-controlling step in the adsorption process.

It is known that there are three consecutive steps in the adsorption of substances by a porous adsorbent. These steps can be expressed as follows (I) film diffusion step (boundary layer) (II) transport of the adsorbate within the pores of the adsorbent except for a small amount of adsorption which occurs on the external surface (particle diffusion) and (III) adsorption of the ingoing adsorbate on the interior surface of the adsorbent[41].

It is generally accepted that process (III) is very rapid and does not represent the rate controlling step. Besides the adsorption at the outer surface of the adsorbents, the solute molecules can also diffuse into the interior of the porous adsorbent. The values obtained from kinetic studies were used in calculating the intraparticle diffusion coefficient.

This was studied by plotting the amount adsorbed (q) *vs.* the square root of time ($t^{0.5}$) (Fig. 4). It is seen that there is an initial curve which is followed by a straight line, indicating that two types of mechanism is operating in the removal of pyridine. The initial curve can be explained by the boundary layer effect while the linear part corresponds to intraparticle diffusion. The rate constants of intraparticle diffusion (k_{int}) for different initial concentration were obtained from the slopes of the straight lines of the curves and were found to be 0.65 and 1.01 mg g^{-1} $min^{-0.5}$ for the initial concentrations of 20 and 35 mg L^{-1}, respectively.

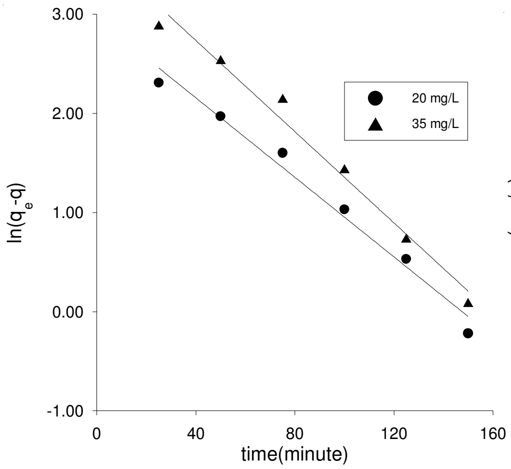

Fig. 3. Lagergren plots for the adsorption of pyridine

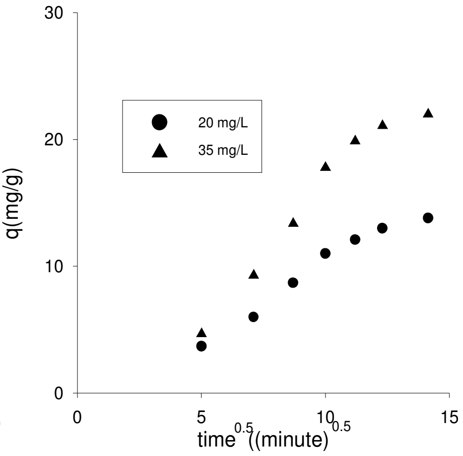

Fig. 4. Intraparticle diffusion for the adsorption of pyridine

The linear portions of the curves do not pass through the origin indicating that intraparticle diffusion is not only rate controlling step for pyridine.

Langmuir isotherm: In order to calculate the adsorption capacity of acid treated spent bleaching earth, the equilibrium data obtained were analyzed using the following linearized equation.

$$C/q = 1/Q_0 b + C/Q_0$$

where C is the equilibrium concentration of pyridine in aqueous solution, q is the amount of pyridine adsorbed per unit weight of the acid treated spent bleaching earth, Q_0 and b are the Langmuir constants. Fig. 5 shows the Langmuir isotherm of the adsorption of pyridine. The values of Q_0 and b were calculated from the slope and intercept of the regression line and were found to be 44.3 mmol g^{-1} and 0.04 L $mmol^{-1}$, respectively.

Giles isotherm: In order to understand the adsorption mechanism, Giles isotherm was used (Fig. 6). According to Fig. 6 the isotherm corresponding to pyridine can be classified as L2 type. The shape of this isotherm indicates that the values of q reach a maximum value.This type occurs in probably the majority of cases of adsorption from dilute solution[42]. The initial curve shows that as more sites in the substrate are filled it becomes increasingly diffucult for a solute molecule to find a vacant site avaliable.

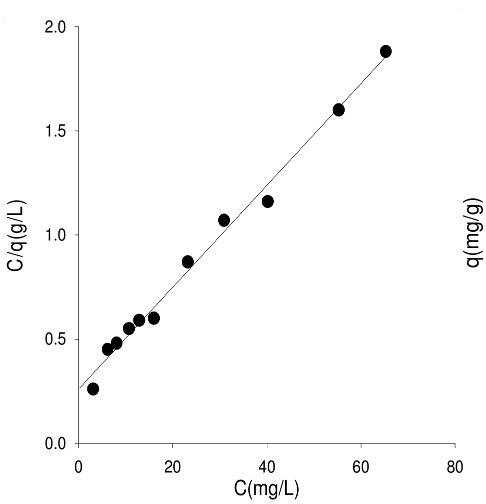

Fig. 5. Langmuir isotherm for the adsorption of pyridine

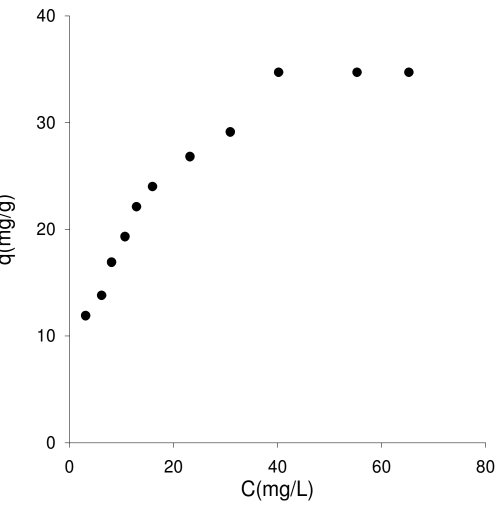

Fig. 6. Giles isotherm for the adsorption of pyridine

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