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Adsorption of β-Picoline on the Adsorbents Produced from Spent Bleaching Earth

MEHMET MAHRAMANLIOGLU
Department of Chemistry, Faculty of Engineering, Istanbul University
Avcilar, Istanbul, Turkey
E-mail: mehmah@istanbul.edu.tr

The sorption of β-picoline by acid treated spent bleaching earth was studied to examine the potentiality of this material in treatment systems. The effect of time, pH, initial concentration on the adsorption of β-picoline was studied. Lagergren first order rate equation was used to describe the adsorption rate of β-picoline and adsorption rate constants were calculated. Rate constants of intraparticle diffusion were calculated. Adsorption isotherms were modelled by the Langmuir equation and the isotherm constants of this isotherm were calculated. The dependence of the adsorption of β-picoline on the pH of the solution was studied to achieve the optimum pH value and a better understanding of the adsorption mechanism. The maximum adsorption was found to occur at pH 7.85. Giles isotherm was used and adsorption type was determined.

Key Words: Adsorption, Spent bleaching earth, β-Picoline, Pyridine.

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].

Picolines are pyridine derivatives. These compounds, which are structural isomers, are obtained from coal tar and petroleum. β-Picoline is used as a solvent in polymers, thermoplastics and fuel chemicals and as a raw material in agrochemicals. β-Picoline is introduced into natural ecosystems as a result of the production of those substances. Many pyridine derivatives 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 immense 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[1-6], biodegradation[7-10], ion exchange[3], ozonation[11], electrochemial oxidation[12].

Among these methods, adsorption processes produce good quality effluents and 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 cost and regeneration costs are high. Therefore, low cost alternatives are being continuously investigated.

In recent years, attention have been devoted to the study of different types of low cost materials such as adsorbents produced from spent bleching earth[13-16], adsorbent produced from agro-industry waste[17], tree fern[18], orange peel[19], montmrollonite[20], chitosan[21], egg shell[22], coal mining waste[23-25], coffee residue[26], brick powder[27], perlite[28], used tires[29,30], biogas slurry[31]. In this study, spent bleaching earth was chosen as a starting material to produce a new adsorbent. Spent bleaching earth (SBE), a solid waste from edible oil processing industry was chosen as a raw material. SBE has two components *i.e.*, residual oil not removed by filter pressing and montmrollonite clay. This material is disposed of directly to landfill option either dry or as a wet slury. But the landfill option causes the problems, the most dangerous being pyrogenic nature of unsaturated oil which rapidly oxidized of the surface to the point of sponteneaous 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 low cost adsorbent. Therefore, in this study SBE was chosen as a raw material to produce a new adsorbent.

In this context, the aim of this study was to investigate the adsorption capacity and adsorption kinetics for removal of β-picoline from aqueous solutions by the adsorbent produced from SBE.

EXPERIMENTAL

All chemicals used in the study were analytical grade. All the solutions were prepared with double distilled water. β-Picoline and all the other chemicals used in the study were obtained from Merck.

Preparation of the adsorbent[32]: 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 SBE into a paste which has been carbonized in a static air muffle furnace in covered crucible 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 were measured by N_2 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.*[32].

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 no significiant changes in the volume of pores. It is also seen from the results for 0-5 mmpore 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.

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

Pore diameter (nm)	Fresh bentonite volume of pores ($cm^3 g^{-1}$)	Absorbent produced from SBE volumes 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

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

Batch experiments: Batch adsorption experiments were carried out using acid treated spent bleaching earth with β-picoline solutions of different glass bottles in a thermostated shaker. Unless otherwise stated, 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 NaCl.

RESULTS AND DISCUSSION

Effect of pH on the adsorption of β-picoline: The pH of the aqueous solution is an important variable which controls the adsorption at the water-adsorbent interfaces. Therefore, the adsorption of β-picoline on acid treated spent bleaching earth was examined at different pH values ranging from 2.72 to 9.12 and presented in Fig. 1. It is seen from Fig. 1 that β-picoline removal increases with increasing pH and the removal of β-picoline is maximum at pH = 7.85. There is no significiantly change in the adsorption of β-picoline between pH 7.85 and 9.12. Similar results were also obtained in some studies[1,2]. Therefore all the other experiments were carried out at pH = 7.85 (± 0.05).

In the low pH region, β-picoline is mostly converted to protonated picoline and the surface of the adsorbent also becomes the positive[1,2]. The strong electrostatic repulsive forces push the particles of β-picoline from the surface of the adsorbent. Therefore, the repulsion between the positively charged β-picoline and the adsorbent surface decreases the adsorption. In the higher pH region, β-picoline is converted to unprotonated β-picoline and the adsorption forces between the adsorbent and β-picoline are mainly dispersion forces and these forces result in the higher adsorption.

Effect of time on the adsorption of β-picoline: Fig. 2 shows that the variation of β-picoline concentration with time. Equilibrium time is 120 and 140 min for the initial concentrations of 25 and 40 mg dm^{-3} and depends on the initial concentrations.

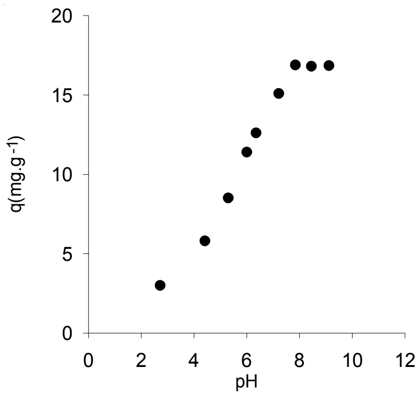

Fig. 1. Effect of pH on the adsorption of β-picoline

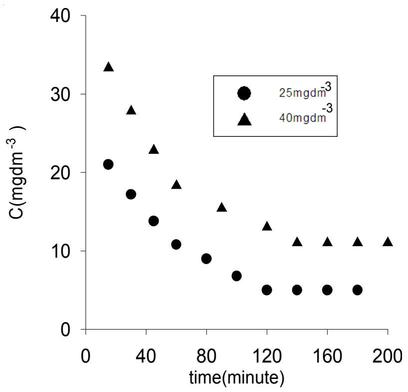

Fig. 2. Variation of concentration with time

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

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

where q and q_e are the amounts of picoline adsorbed at time t and equilibrium, respectively, k is the rate constant. The linear plots of ln (q_e – q) *vs.* time show the applicability of this equation and the values of k were calculated from the slope of straight lines and found to be 0.025 and 0.022 min^{-1} for the initial concentrations of 25 and 40 mg dm^{-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[32].

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 picoline. 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 1.62 and 1.74 mg g^{-1} $min^{-0.5}$ for the initial concentrations of 25 and 40 mg dm^{-3}, respectively.

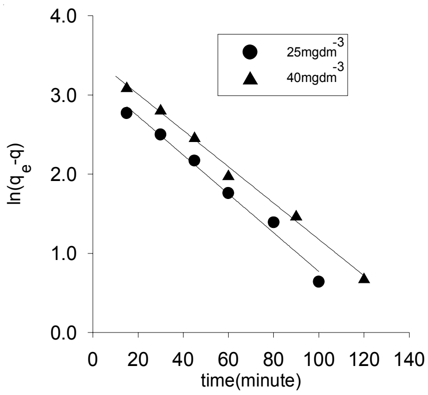

Fig. 3. Lagergren plots for the removal of β-picoline

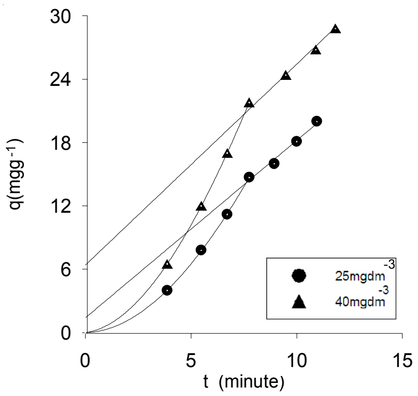

Fig. 4. Intraparticle diffusion for the adsorption of β-picoline

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

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.

$$C/q = 1/Q_O\, b + C/Q_O$$

where C is the equilibrium concentration of β-picoline in aqueous solution, q is the amount of β-picoline adsorbed per unit weight of the acid-treated spent bleaching earth, Q_O and b are the Langmuir constants. Fig. 3 shows the Langmuir isotherm of the adsorption of β-picoline. The values of Q_O and b were calculated from the slope and intercept of the regression line and were found to be 41.7 mmol g^{-1} and 0.25 dm^3 $mmol^{-1}$, respectively.

Giles isotherm: In order to understand the adsorption mechanism, Giles isotherm was used (Fig. 5). According to Fig. 5 the isotherm corresponding to β-picoline can be classified as L2 type. This type occurs in probably the majority of cases of adsorption from dilute solution[33]. The initial curvature shows that as more sites in the substrate are filled it becomes increasingly difficult for a solute molecule to find a vacant site avaliable.

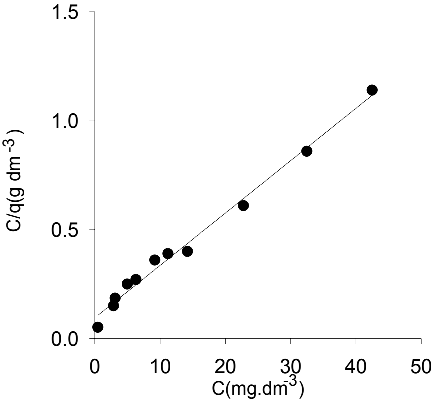

Fig. 5. Langmuir isotherm for the adsorption of β-picoline

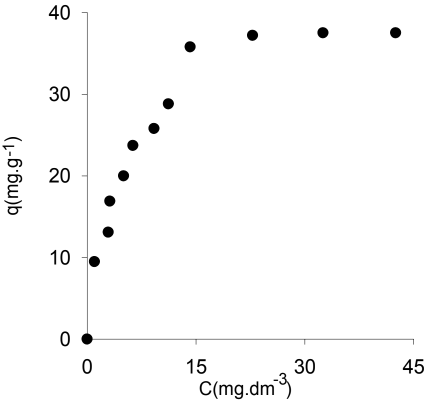

Fig. 6. Giles isotherm for the adsorption of β-picoline

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