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Adsorption of α-Picoline and γ-Picoline on the Adsorbent Produced from Spent Bleaching Earth

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Adsorbents were produced from spent bleaching earth and the individual adsorption of α-picoline and γ-picoline by them was studied as a function of time, pH and initial concentration. The adsorption process for both solutes followed the first order Lagergren equation and the rate constants of the adsorption were calculated for each solute. Rate constants of intraparticle diffusion were also calculated for each solute. The adsorption capacities were obtained from the Langmuir isotherm. In order to understand adsorption mechanism, Giles isotherm was used and adsorption type for each solute was determined. Maximum adsorption capacity was observed between pH: 8.13 and 8.77.

Key Words: α-Picoline, γ-Picoline, Adsorption, Spent bleaching earth.

INTRODUCTION

Pyridine is widely used as a solvent and intermediate in the production of pipiridine, agricultural chemical drugs, dyestuffs, paints, rubber products, polycarbonate resins and textile water repellents[1,2]. α-Picolines and γ-picolines (pyridine derivatives) are useful as solvent and as raw material for various chemical products used in the industries such as polymers, textiles, fuels, agrochemicals and pharmaceuticals[1].

Many of pyridine derivative compounds are hazardous in nature and persist for a longer duration in the environment. Therefore, removal of pyridine derivatives from a water stream is of great importance. In order to remove pyridine and picolines, many methods such as adsorption[1-6], biodegradation[7-10], ion exchange[6], ozonation[11], electrochemical oxidation[12] have been used. Among these methods, adsorption is a promising method since adsorption processes produce good quality effluents and is a very effective process.

Activated carbon has been used extensively as an adsorbent in treatment systems since it has a high surface area and good porosity. However, activated carbon has some disadvantages, since its price and regeneration cost are high. Therefore, low cost alternatives are being continuously investigated. A number of materials including activated carbon produced from agricultural waste materials[1,2,4,13,14], rundle-spent shale[15-17], clay minerals[3,18,19], activated kaolinite[3,5], zeolite[20], ion exchange resins[6] and adsorbent from spent bleaching earth (SBE)[21] have been reported for the removal of pyridine and its derivatives from water.

In our laboratory, new adsorbents have been produced from cheap materials such as used tyres[22,23], SBE[24-26], coffee residue[27] and contaminated soil[28]. The adsorbents produced from those materials have shown high capacities for some organic and inorganic pollutants.

In order to understand the capacity of the adsorbents from those materials, it is necessary to use them in removal of different pollutants. Therefore, in this study, spent bleaching earth (SBE) was chosen as a starting material to produce a new adsorbent. SBE is a solid waste from edible oil processing industry and has two components: (a) residual vegetable oil not removed by filter pressing and (b) montmorillonite clay. This material is disposed of directly to landfill either dry or as a wet slurry. But the landfill option causes problems, the most dangerous being the pyrogenic nature of the unsaturated oil which rapidly oxidises on clay surface to the point of spontaneous ignition.

A good solution from an environmental and economic standpoint is its application in the waste water industries as low cost adsorbent after suitable regeneration process[29]. The aims of this study were (1) to develop a new adsorbent and to show its adsorption capacity for removal of α-picoline and γ-picoline and (2) to minimize pollution from oil industry.

EXPERIMENTAL

Preparation of adsorbent: Impregnation with 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.*[30].

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 comparison of the activated bentonite and adsorbent produced from SBE that there is no significant 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.

TABLE-1
PORE DISTRIBUTION FOR FRESH BENTONITE AND ADSORBENT PRODUCED FROM SBE

Pore diameter (mm)	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

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

Adsorption experiments: All the solutions were prepared using double distilled water. α-Picoline and γ-picoline were obtained from Merck. The pH of the solutions was adjusted either with 0.01 N HCl or 0.01 N NaOH.

Batch adsorption experiments were carried out at 20 ºC by shaking a known amount of adsorbent and α-picoline or γ-picoline solutions of desired concentrations and pH in different glass flasks in a shaking thermostat machine. At the end of predetermined time intervals, samples were withdrawn and centrifuged. The concentrations of α-picoline and γ-picoline were determined using spectroscopic method.

RESULTS AND DISCUSSION

Effect of pH on adsorption of α-picoline and γ-picoline: The pH of the aqueous solution is an important variable which controls the adsorption at the water-adsorbent interfaces.

Therefore, in order to understand the effect of pH on the adsorption of α-picoline and γ-picolines, the removal of α-picoline and γ-picoline as a function of pH was studied at different pH ranging from 2.72 to 8.77 for them (Fig. 1). Adsorption process did not affect the pH of the solution in acidic region. However, in basic region the equilibrium pH of the solutions decreased by 0.2 or 0.25 unit. Therefore, pH of the solution in basic region were adjusted during the adsorption process.

With change in pH of the solution from acidic region to basic region, the removal of α-picoline and γ-picoline increases. The adsorption is an

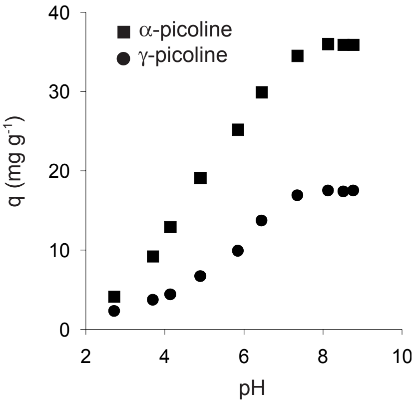

Fig. 1. Change of the adsorption of α-picoline and γ-picoline with pH (initial concentrations for each solute = 50 mg dm^{-3})

extremely complex process. In the low pH region, α-picoline and γ-picoline are mostly converted to protonated picolines[1] and in this region the surface of adsorbents also become more positive. The strong electrostatic repulsive forces push the particles of α-picoline and γ-picoline from the surface of the adsorbent. Therefore, the repulsion between the positively charged α-picoline and γ-picolines and the adsorbent decreases the adsorption.

It is seen from Fig. 1 that maximum adsorption for both solute was obtained in the pH range 8.13-8.77. Therefore, all the studies were carried out at pH 8.13 (± 0.05).

In the higher pH region, α-picoline and γ-picoline are converted to unprotonated α-picoline and γ-picoline and the adsorption forces between the adsorbent and α-picoline and γ-picolines are mainly dispersion forces which resulted in the higher adsorption. These results show that the dominant mechanism for the adsortion of the α-picoline and γ-picoline is van der Waals forces. Similar results were reported by Mohan *et al.*[1].

Effect of time on adsorption of α-picoline and γ-picoline: The time dependence curves of adsorption of α-picoline and γ-picoline are shown in Figs. 2 and 3. It is seen from these figures that the adsorption of the solute is fast in the first 1 h. Equilibrium time for the initial concentrations of 30 and 50 mg dm^{-3} is 130 and 185 min for α-picoline and γ-picoline, respectively.

These results show that the equilibrium time for both solutes depends on the initial concentration and not on the type of solute.

Adsorption kinetics: The adsorption rate constants of α-picoline and γ-picoline were determined from the following Lagergren equation:

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

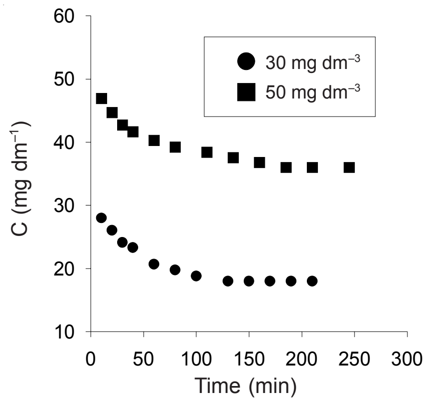

Fig. 2. Variation of concentration of α-picoline with time

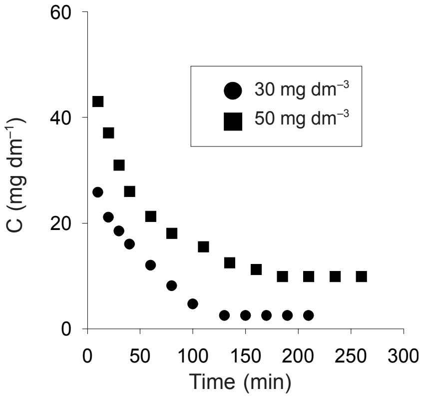

Fig. 3. Variation of concentration of γ-picoline with time

where q_e and q (both in mg g^{-1}) are the amount of α-picoline and γ-picoline adsorbed per unit mass of adsorbent at equilibrium and time (t), respectively and k_a is the rate constant (min^{-1}). The value of k_a was calculated from the solute slope of linear plot of ln (q_e-q) against time (Figs. 4 and 5). The adsorption rate constants for the initial concentrations of 30 and 50 mg dm^{-3} are given in Table-2.

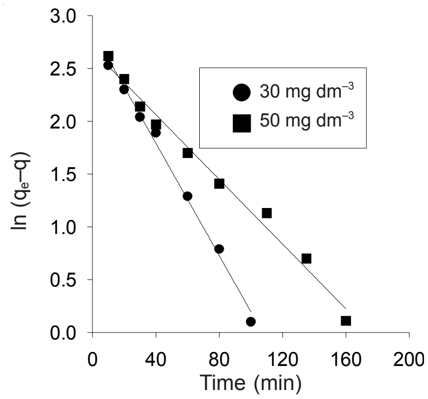

Fig. 4. Lagergren plots for α-picoline

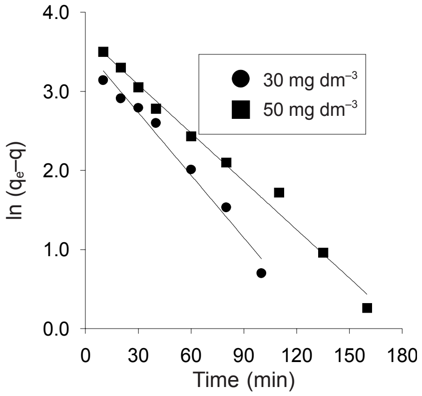

Fig. 5. Lagergren plots for γ-picoline

TABLE-2
CONSTANTS OF LAGERGREN EQUATION, INTRAPARTICLE DIFFUSION AND THE LANGMUIR ISOTHERM

	Lagergren constant k_a (min^{-1})		Intraparticle constants k_{int} (mg g^{-1} $min^{-0.5}$)		Langmuir constants	
	30 mg dm^{-3}	50 mg dm^{-3}	30 mg dm^{-3}	50 mg dm^{-3}	Q_0 (mg g^{-1})	b(mg g^{-1})
α-Picoline	0.259	0.017	0.922	0.962	21.73	0.121
γ-Picoline	0.264	0.202	1.953	2.054	78.89	0.232

Intraparticle diffusion: In the adsorption processes, there are three consecutive steps: (1) film diffusion step, (2) transport of adsorbate within the pores of the adsorbent, and (3) adsorption of the ingoing adsorbate on the interior surface of the adsorbent[31].

It is generally accepted that process 3 is 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.

In order to calculate the rate constant of intraparticle diffusion, the following equation was used.

$$q = k_{int}\, t^{1/2}$$

where k_{int} (mg g^{-1} min$^{-0.5}$) is the intraparticle diffusion rate constant. Figs. 6 and 7 show that there is an initially curved portion and the subsequent linear portion. The former indicates the film diffusion and the latter indicates the intraparticle diffusion. The values of k_{int} were obtained from the slope of linear portion of the curve for each solute. The values of k_{int} for α-picoline and γ-picoline are given in Table-2.

The linear portion of the curves do not pass through the origin indicating that intraparticle diffussion is not only rate controlling step for all the solutes. Figs. 6 and 7 shows that both the film diffusion and intraparticle diffusion contribute to the rate determining step.

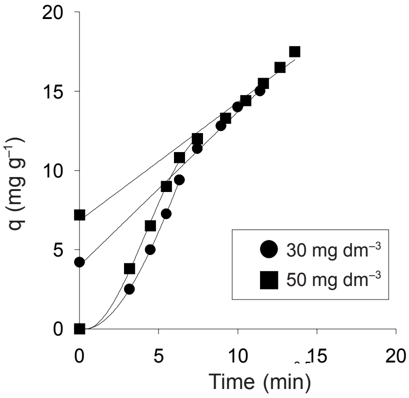

Fig. 6. Intraparticle diffusion for α-picoline

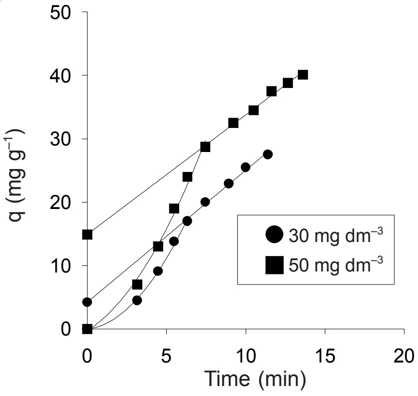

Fig. 7. Intraparticle diffusion for γ-picoline

Adsorption isotherm: In order to quantify adsorption capacity for both solutes, Langmuir equation was applied. This equation can be given as follows:

$$C/q = C/Q_0 + 1/Q_0b$$

where C and q are equilibrium solute concentration (mg dm^{-3}) and equilibrium adsorption capacity, respectively (mg g^{-1}). Q_0 and b are the Langmuir constants representing adsorption capacity (mg g^{-1}) and energy of adsorption (dm^3 mg^{-1}), respectively.

The value of Q_0 and b were calculated from the slope and intercept of the linear plot of C/q *vs.* C (Figs. 8 and 9) and are given in Table-2. It is seen from the results that the values of Q_0 followed the order of

γ-picoline > α-picoline

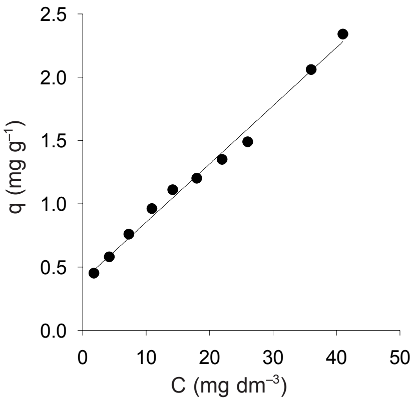

Fig. 8. Langmuir isotherm for the adsorption of α-picoline

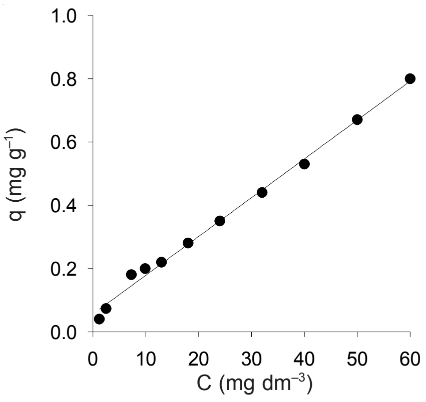

Fig. 9. Langmuir isotherm for the adsorption of γ-picoline

The adsorption of β-picoline on the same adsorbent and the value of Q_0 for β-picoline was found to be 41.7 mg g^{-1}. If we reorder all these results, the values of Q_0 follow the order as γ-picoline > β-picoline > α-picoline.

It is concluded that steric hindarance occurs between the CH_3 group attached to the heterocyclic ring and the nitrogen group restricts the adsorption of α-picoline. In the case of β-picoline the steric effect does not restrict the adsorption capacity significantly and in the case of γ-picoline steric effect is not seen.

Therefore, the maximum adsorption was found in the case of γ-picoline followed by β-picoline and α-picoline. Similar results were obtained by Mohan *et al.*[1].

Giles isotherm: Figs. 10 and 11 show the Giles isotherms for α-picoline and γ-picoline. According to Giles classification in the case of α-picoline, the shape of the obtained isotherm shows L2 isotherm and in the case of γ-picoline, the shape of obtained isotherm shows H2 isotherm.

These results show that Giles isotherms for both solutes have the same subgroups 2. But the meaning of L and H curves is very different. In the L2 curve, the slope of the initial curve steadily falls with rise in concentration

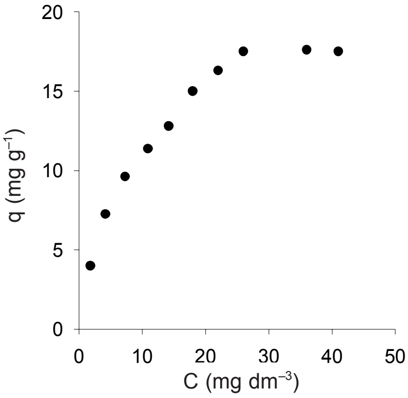

Fig. 10. Giles isotherm for the adsorption of α- picoline

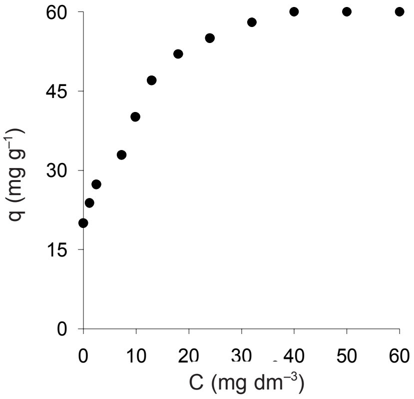

Fig. 11. Giles isotherm for the adsorption of γ-picoline

because vacant sites become more difficult to find with the progressive covering of the surface and eventually the slope becomes zero at the saturation point, when no vacant sites remain[32].

In the case of γ-picoline the initial curve shows that sites in the substrate are filled and it becomes increasingly difficult for a bombarding solute molecule to find a vacant site available and it is impossible to find a vacant site in the region of plateau.

H curve is a special case of the L curve, in which the solute has a high affinity than in dilute solutions. It is completely adsorbed[33] and the first portion of the curve changes abruptly to a flat plateau.

In the case of γ-picoline, the adsorbent can remove γ-picoline completely in the region of dilute concentrations and a saturation point is also seen in the beginning of the plateau.

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