CERTIFICATE

This is to certify that the dissertation entitled

Adsorption of 2-Naphthol from Aqueous Solutions on Amberlite XAD-4

is the bonafide record of research work done by

Mr. Cheo Yoke Yeong

during the period of 17th December 2006 to 2nd May 2007 under my supervision.

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Cheo Yoke Yeong
(78008)

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Abstract

2-naphthol is a hazardous chemical and its exposure is possible in our routine life. To minimize the effects of its exposure, its adsorption on suitable adsorbents is necessary. In this work, batch equilibrium studies have been conducted to remove the pollutant from aqueous solutions onto Amberlite XAD-4 resin. The effect of pH (2, 4, 6 and 8), shaking time (15, 30, 45 and 60 min), the concentration of substance (0.0010, 0.0015, 0.0020, 0.0025, 0.0030 M) and the amount of adsorbent (0.5, 1.0 and 1.5 g) on percent adsorption of 2-naphthol has been investigated. The concentration of 2-naphthol has been monitored on a UV-visible spectrophotometer at 273 nm detection. From the experiment, the optimized condition for adsorption of 2-naphthol onto Amberlite XAD-4 are pH (2), agitation time (60 min), concentration (0.0010M) and amount of adsorbent (1.5 g). The data also fits to the sorption dynamic module (Lagergren equation and Morris-Weber equation) and sorption isotherm module (Freundlich isotherm, Langmuir isotherm, and Dubinin-Radushkevich (D-R) isotherm).

Introduction

2-naphthol also can be named as β-hydroxynaphthalene , β-naphthyl alcohol , Azogen Developer A , C.I. Azoic Coupling Component 1 , C.I. Developer 5 , Developer AMS , Developer BN , Isonaphthol , (beta)-naphthol, (beta)-hydroxynaphthalene and isonaphthol. (1) The chemical formula is C10H8O and molecular mass is 144.2.

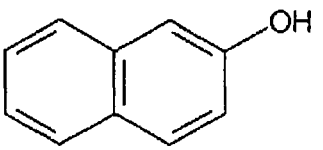

Figure 1: Structure formula

According to Organisation for Economic Cooperation and Development (OECD), Screening Information Data Set (SIDS) Initial Assessment Report for Society for Industrial and Applied Mathematics (SIAM) the worldwide production capacity of 2-naphthol is approximately 100,000 metric tonnes per year. The substance is used as an intermediate for the production of dye-stuffs, pharmaceuticals, fungicides, insecticides and odor agents. The substance is also used as an antioxidant for rubber and plastic, grease and lubricants. Releases into the environment may occur during production and processing of 2-naphthol and from its direct use as e.g. antioxidant. Further sources are the waste water from the conversion of coal to liquid and gaseous fuel products , the waste water of the petroleum industry , and the groundwater near waste sites from wood-treatment processes. From here, we can realize the close relationship of 2-naphthol with our daily life and the threat of its exposure.

Consumers may be exposed to 2-naphthol through cigarette smoke (Commins and Lindsey, 1956). Traces of 2-naphthol were detected in bottled mineral water (0.2 - 2.9 µg/l); the source of this contamination was identified as the red colored plastic caps (Manninger, 2001). In the European Union, 2-naphthol is listed as a substance which must not form part of the composition of cosmetic products (EC, 1999). The marketing of medicines contain 2-

naphthol, e.g. for the treatment of warts, is prohibited in Germany (AMK, 2001). In four out of 79 farm workers that were treated for hookworm infection with 6 g of 2-naphthol (of unknown purity) for 3 days, haemolytic reactions resulting in severe anaemia, spleen and liver enlargement and haemoglobinuria were seen. Three out of the 4 workers had suffered from malaria beforehand (Smillie, 1920).

It is classified as hazardous chemical by causing irritation to skin, eyes and respiratory tract if swallowed or inhaled. Another health effects from exposure to this substance is skin irritation including redness, itching, and pain. It causes cough and sore throat when a harmful concentration of airborne particles can be reached quickly when dispersed. The substance is severely irritating to the eyes and redness, pain, or blurred vision (lens opacities) might be happened in serious case. Through ingestion pathway, 2-naphthol can trigger the abdominal pain, nausea (anemia), vomiting, and diarrhea. The waste should not be thrown away into usual sanitary system as it is very toxic to aquatic organisms. 2-naphthol will flow into river follow the path of draining system. The threat to the aquatic population is possible in contaminant area even it is diluted by large amount of water. Also remember, for anyone who consumes the fish in that area, they are exposed to the health's risk by ingestion pathway and cause symptoms mention above. in order prevent vicious cycle continue in our daily life, the substances must be treated with proper waste control guidelines. (IPCS, 2005))

Amberlite XAD-4 is a cross-linked styrene-divinyl-benzene polymer and is non-polar and very hydrophobic. Compared with classical adsorbents, such as silica gels, aluminas and the activated carbons, the macro-porous polymers is more attractive alternative because of the wide range of pore structures and surface characteristics (Kunin et al., 1976). The use of these polymeric adsorbents for the treatment of effluents containing benzoid compounds has been widely studied (Xu et al., 1997). XAD-4 is always used as a filter in many research investigations due to its adsorptive properties. It has high surface area (> 750 $m^2 g^{-1}$) and effective adsorption even in small amount. Another characteristic of XAD-4 is its porosity (> 0.50 mm) and can be used for very tiny particle analytes. The excellent physical properties of Amberlite XAD-4 result due to its patented macroreticular structure containing both a continuous polymer phase and a continuous pore phase. This structure is known as a non-ionic cross linked polymer. The white translucent beads also has good chemical property because it can be used in different type of chemical solution without interfering the reaction

results. Another reason the macroreticular crosslinked aromatic polymer becomes a major choice in adsorption process is it has good thermal stability (~ 150°C).

According to Rohm and Haas' information, XAD-4 can be used to remove the organic pollutants from aqueous wastes, ground water, and vapor streams or aqueous process streams and polar solvent. Meanwhile, some user favors to utilize it to recover or recycle the phenolic and aromatic compounds. Also, it also can recover the organic compounds in environmental and clinical analysis for subsequent identification. Another application of XAD-4 is to remove the chlorinated solvent, herbicides, and pesticides form aqueous streams.

The recommended range of pH and temperature XAD-4 can withstand, has been suggested by Rohm & Hass (USA), i. e. pH (0 – 14) and T (150°C). This information is essential for the efficient use and regeneration of the resin after adsorption experiments.

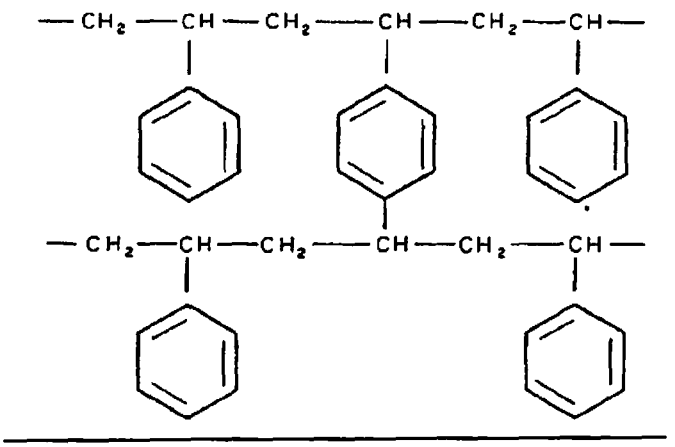

Figure (2): chemical structure of XAD-4

Literature review

Evan et al., (1975) used XAD-4 to remove the phenol in industrial waste stream by passing through it. Regeneration of the resin could be effected by an acetone or MeOH treatment. Acetone for recycle in the regeneration step and phenol (99% purity) could be recovered by distillation.

The sorption potential of treated rice husk for the removal of 2,4-DCP from aqueous solutions has been investigated (Akhtar et al., 2006). The kinetics and thermodynamic parameters were evaluated. The sorption data obtained at optimized conditions was subjected to Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms. Lagergren and MOrris-Weber equations were employed to study kinetics of sorption process.

Pletrzyk et al., (2004) employed Amberlite XAD-4 in reversed-phase chromatography to evaluate it as the stationary phase for preparative liquid chromatography.

Baytaki et al., (2004) determined manganese in alloys after preconcentration onto Amberlite XAD-4 loaded with Saccharomyces and determination by flame AAS. Turk J. Chem., 28 (2004) 243-253.

Shahtaheri et al., (2006) used XAD-4 to retain cadmium .

Lee et al., (1983) showed that in the adsorption of 8-hydroxyquinoline onto XAD-4, the resin was stable pH range from 6.0 to 10.0 and eluted sorbent when treated with hydrochloric acid was negligible. 8HQ-impregnated-XAD-4 resin could be reusable over 5 times without decrease in its impregnation capacity.

Li et al., (2001) used acetylated derivative resin to comparatively evaluate four phenolic compounds and showed 20 % increase in the capacities of equilibrium adsorption than

untreated resin within temperature range of 283-323 K. Qourzal et al., (2004) showed that organic pollutant, 2-naphthol can degrade and decrease activated carbon's adsorption strength in shorter time.

Robert (1976), stated that the ideal waste treatment process would be one that would remove the phenol from the waste and would recover the phenol in a usable form is Amberlite XAD-4.

Roets et al., (2001), extracted XAD-4 with water in preliminary purification and washed and eluted with acetonitrile. Turker et al., (2004) immobilized Escherichia coli on Amberlite XAD-4 and used as a solid-phase extractor

Xu et al., (1997) had studied the adsorption of I-naphthol, 2- naphthol, I-naphthylamine and 2- naphthylamine from aqueous solutions on macroporous polymeric adsorbents. The equilibrium data were fitted to Freundlich-type isotherms and the equilibrium constauts K, and n were obtained. The values of the adsorption capacity depend on the surface area of adsorbents, the chemical properties of naphthalene derivatives, as well as the polarity of adsorbents.

Objectives

1) To remove 2-naphthol from aqueous solution onto Amberlite XAD-4.

2) To investigate the effect of pH, shaking time, concentration of solution and amount of adsorbent on the adsorption of 2-naphthol onto XAD-4.

3) To investigate the kinetics and thermodynamics of adsorption of 2-naphthol onto XAD-4.

Materials

Glassware

Beaker 25ml, beaker 100 ml, beaker 500 ml, 100 ml volumetric flask, 1000 ml volumetric glass, glass bowl, 10 ml cylinder measurement, 25 ml measurement cylinders, 100 ml measurement cylinders, measurement 10 ml,

Equipments

pH 211 Microprocessor pH meter, Heidolph rotamax 120, Cary 100 UV spectrometry, , Dragon 204 weight machine, Memmert hot air oven, Whatmann filter paper no. 44. A 10 µl

Chemical reagents

Acetonitrile, 1.0 M HCl and 2-Naphthol (Merck company)

Diethyl ether, and methanol (R&M Marketing)

1.0 M NaOH (BDH Laboratory Supplies Poole)

2.0 Milli-Q water (Unit Kemudahan Makmal, USMKK)

Methodology

Sample preparation

XAD-4

As mentioned in literature review part, raw xad4 is water wet product that has sodium chloride NaCl) and sodium carbonate (Na2CO3) salts imbibed with it in term of retarding the bacterial growth in its shipping. Before it is used for experiment, we should wash away these compounds so that it would not interrupt the chemical process. The UV detection will show a wrong, extra, undesired result which hardly can be interpreted and convey a wrong message in this research.

1. XAD-4 has been washed with Solxphet extraction method.
2. Firstly, it is treated with methanol for 4 hours.
3. Then, it is washed with acentonitirl and diethyl ether respectively for 4 hours
4. It is left for drying.

2-naphthol solution

Different factors of experiment condition are set up to find out the optimum condition of XAD-4 that can carry out the adsorption process effectively. The solubility of 2-anphthol in water is 0.07 mg/L and the concentration of sample is 1×10^{-3} which mean 0.0144 mg/L So, a little amount of methanol is added to make it soluble before distilled water is filled up the remaining amount.

Parameters

pH effect: pH 2, 4, 6, and 8 are adjusted and studied its influence upon the adsorbent by mixing it together.

Shaking time: after find out the optimum pH that best for adsorption process, the pH will be used in this second phase. Shaking time 15 minutes, 30 minutes, 45 minutes and 60 minutes are studied.

Amount of absorbent: 0.5 g, 1.0 g and 1.5 g have been carried out to observe the relationship between amount of absorbent and adsorption power.

Each pH solution is prepared in 500 ml stock. pH is adjusted with hydrochloric acid and sodium hydroxide

Sample running:

To make this research do it in quickest way, I divided it into 4 batches according to shaking time (15 minutes, 30 minutes, 45 minutes, and 60 minutes) so that every sample can be run in the same time track and would not waste any time in waiting.. The first batch is 15 minutes which has 4 groups. These four groups are pH 2, pH 4, pH 6, and pH 8 that I prepared 1 liter each. After that, the amount of XAD-4 is weighted about 0.5 g, was added to the solution. Then, it is shaken 15 min with agitation speed 100 rpm. The procedures were preceded with agitation time 30 min, 45 in, 60 min. Subsequently, it was taken to UV spectrometry for absorbance. After we obtain the optimized information about the pH and agitation time, it will be used for next parameter experiment, which was concentration (0.0010M, 0.0015M, 0.0020M, 0.0025M, and 0.0030M). When an optimized condition of concentration was confirmed, with optimized pH and agitation time, these conditions will be used to investigate the parameter, amount of adsorbent (0.5 g, 1.0 g, and 1.5 g). All the experiments were performed in triplicate.

According to Akhtar (2006), the sorbed concentration of sorbate on sorbent surface was calculated by the difference in the detection response peak height (% adsorbance) before and after shaking. The % sorption and distribution coefficient were calculated by Eqs, (1) and (2), respectively, as follow:

$$\% \text{ sorption} = (Ci - Ce)/ Ci \times 100 \qquad (1)$$

$$Rd = (\text{amount of analyte in rice husk}/ \text{amount of analyte in solution}) \times V/ W \qquad (2)$$

where Ci and Ce are the initial and equilibrium concentrations (mol L^{-1}), respectively, of sorbate; Rd is the distribution coefficient, V is the volume of the solution (cm^3); and W is the weight of XAD-4 (g)

Correlation among % sorption and the distribution coefficient may be located by the following equation:

$$\% \text{ sorption} = 100\ Rd/ (Rd + (V/ W)) \qquad (3)$$

Nomenclature

- qe: the equilibrium concentration at time, t
- qt: the sorbed concentration at time, t
- R2: coefficient of determination
- Cads: the sorbed concentration of sorbate onto sorbent in solution
- Ce: equilibrium concentration of sorption in solution
- Ci: initial concentration of sorption in solution
- ε: Polanyi sorption potential with equation

$$\varepsilon = RT.\ln (1 + (1/ Ce))$$

R is a gas constant in kJ mol^{-1} K^{-1}, t is the temperature in Kelvin, and Ce is the equilibrium concentration of sorbate in solution (mol L^{-1})

All the formulas and equations in this paper are referred to Akhtar (2005).

Results and Discussion

Standard	pH 2	pH 4	pH 6	pH 8
Ci	3.3856	3.3940	3.3620	3.4057

Table (1): UV absorbance of standard solution. (before agitation time)

Agitation time (min)	pH	λ max, Ce	Agitation time (min)	pH	λ max, Ce
15	2	0.2086	45	2	0.0684
	4	0.3219		4	0.0874
	6	0.4437		6	0.0793
	8	0.3857		8	0.0669
30	2	0.0979	60	2	0.0410
	4	0.1345		4	0.0702
	6	0.1142		6	0.0422
	8	0.1652		8	0.0566

Table (2): UV absorbance of solution after treated with agitation process in each different time.

% adsorption = 100 (Ci – Ce)/ Ci

Agitation time (min)	pH	% adsorption	Agitation time (min)	pH	% adsorption
15	2	93.84	45	2	98.34
	4	90.52		4	97.39
	6	86.80		6	98.01
	8	88.67		8	98.24
30	2	97.11	60	2	98.78
	4	96.04		4	97.04
	6	96.60		6	98.74
	8	95.15		8	98.33

Table (3): Percentage of adsorption under effect of pH and agitation time.

From agitation time data, the constant equilibrium still had not achieved. In order to figure out optimized agitation time, the investigation was conducted on 75 min and 90 min agitation time.

pH: 2
Ci: 3.3555
Concentration: 1 x 10-3 M
Temperature: 25 °C
Amount of adsorbent: 0.5 g

Agitation time (min)	Ce	% adsorption
60	0.0410	98.78
75	0.0473	98.59
90	0.1069	96.81

Table (4): Percentage of adsorption under the effect of 60 min, 75 min, and 90 min agitation time.

From the experiment data, we can illustrate four graphs of pH and four graphs of agitation time regarding percentage adsorption.

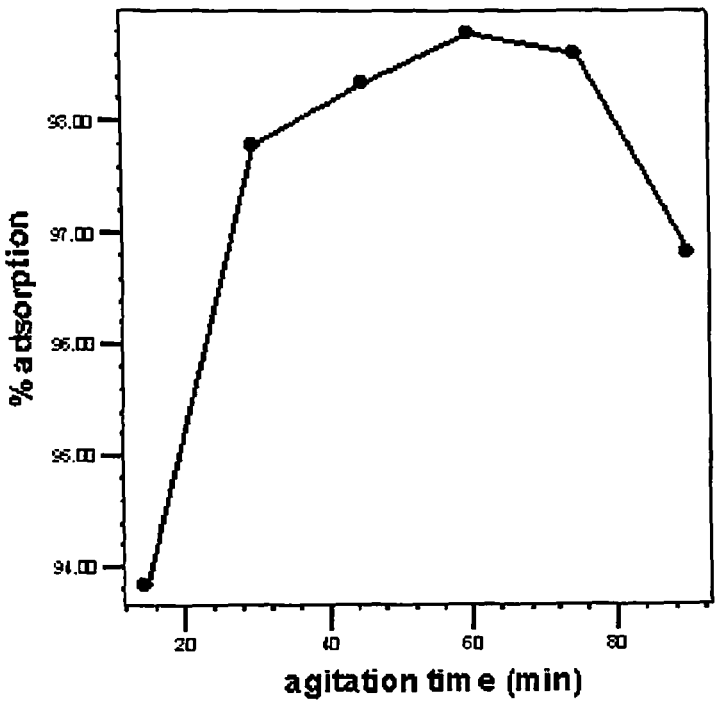

Figure (3): % adsorption of pH 2 on different agitation time (min)

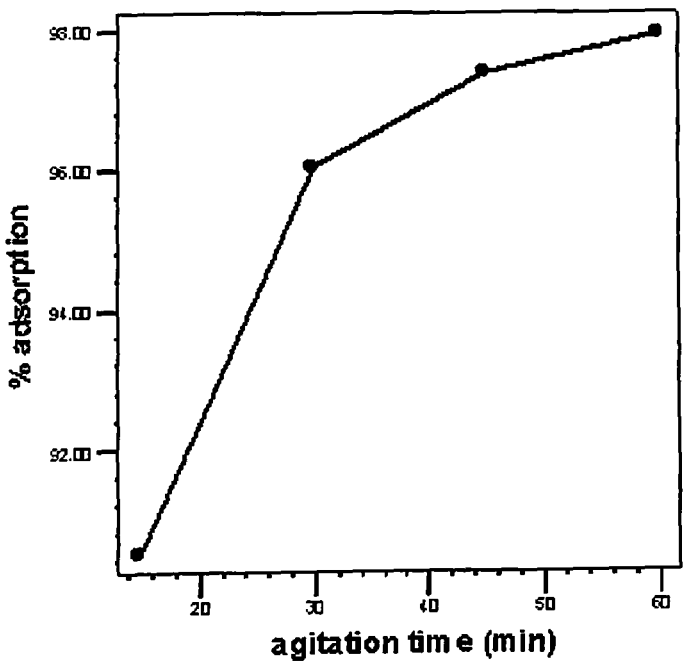

Figure (4): % adsorption of pH 4 on different agitation time (min)

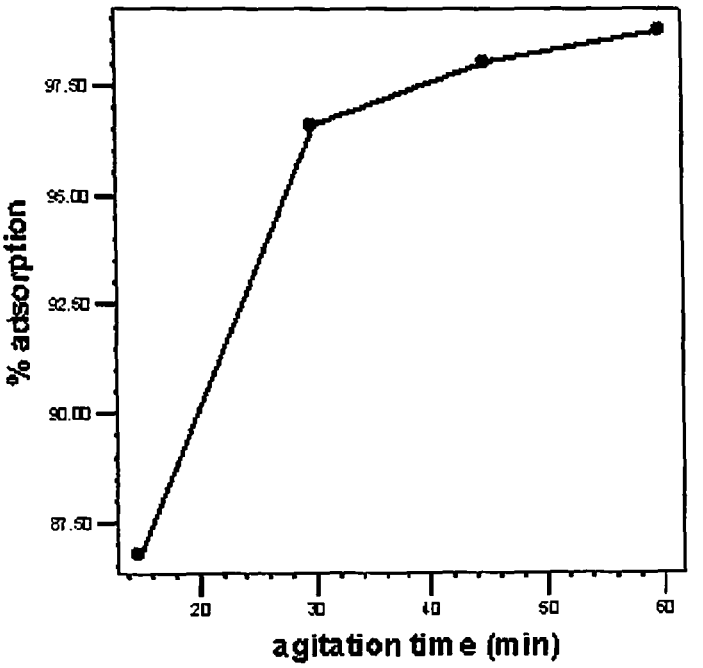

Figure (5): % adsorption of pH 6 on different agitation time (min)

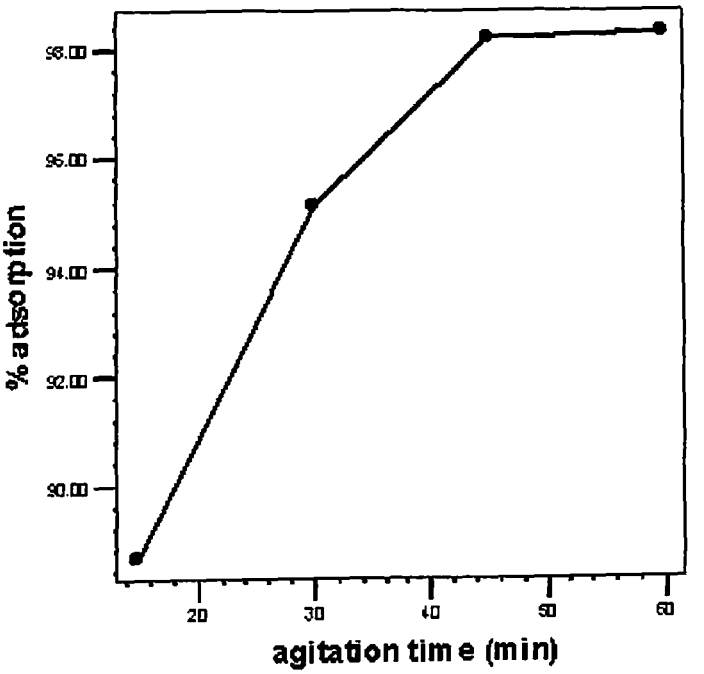

Figure (6): % adsorption of pH 8 on different agitation time (min)

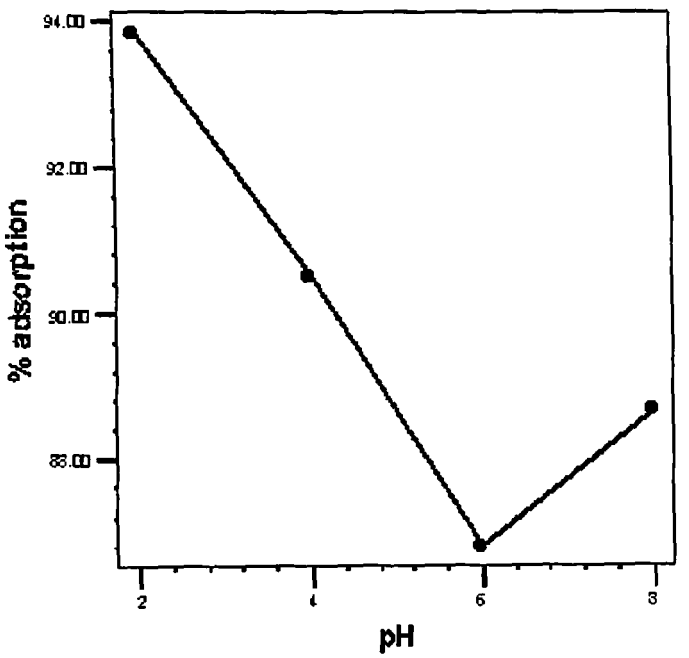

Figure (7): % adsorption of 15 min agitation time on different pH

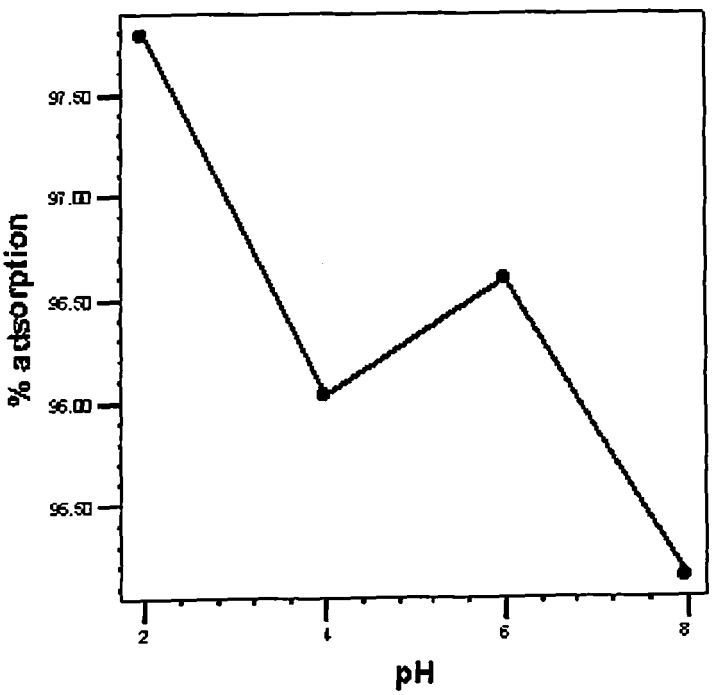

Figure (8): % adsorption of 30 min agitation time on different pH

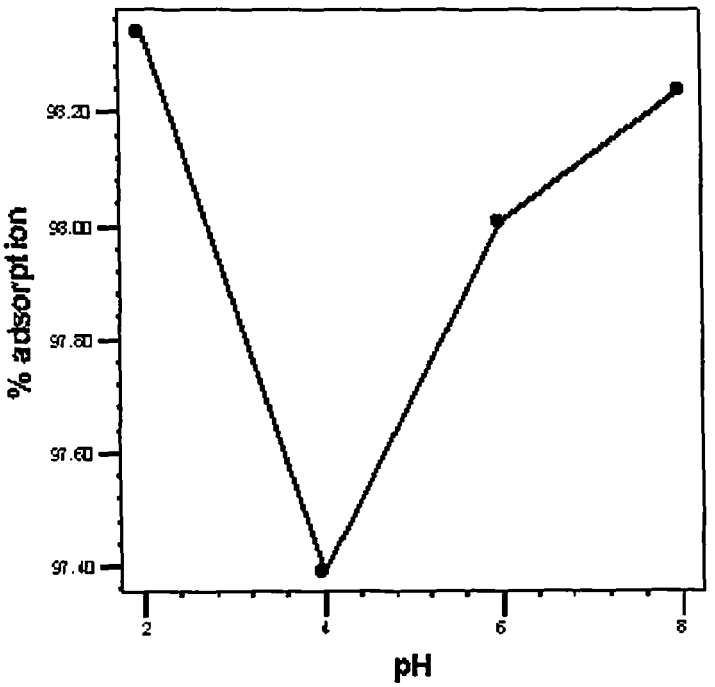

Figure (9): % adsorption of 45 min agitation time on different pH

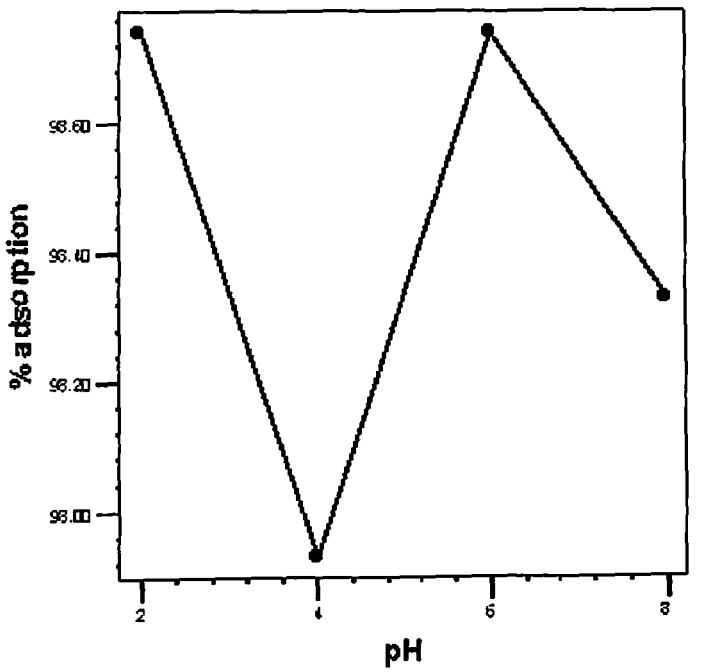

Figure (10): % adsorption of 60 min agitation time on different pH