WASTEWATER TREATMENT USING MODIFIED ALUMINA

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ABSTRACT

Alumina surface was modified by adsorption of an anionic surfactant, sodium sulfate (S.S). Typical S-shaped isotherm of surfactant on alumina was observed. The adsorption of herbicide on alumina and surfactant treated alumina has been investigated. The enhancement in adsorption of herbicide on surfactant treated alumina is observed, which may be attributed to the solubilization of herbicide on surfactant aggregates formed at solid/liquid interface. The effect of pH on adsorption has been studied. The adsorption is greatly influenced by pH of the medium. The applicability of Freundlich equation was tested for equilibrium data. The influence of various factors such as initial concentration, and mass of adsorbent on adsorption was also studied. The batch kinetics has been tested to pseudo second order reaction and rate constants were calculated.

KEYWORDS

Waste water, surfactant, alumina

LIST OF ABBREVIATIONS

Sodium sulfate	S.S
Hemi-micellar concentration	HMC
Critical-micellar concentration	CMC
Equilibrium concentration	q_e
Frendlich constant	K_f

INTRODUCTION

The removal and disposal of waste pesticides and other organic compounds are one of the most important problems concerning modern agricultural activities today [1]. Pesticides and their metabolites have been reported in drinking water, agricultural water and aquatic organisms since 1945 [2]. The pollution of the water environment with pesticides is effected through their use in the control of aquatic weeds and insects; leaching and run-off from agricultural and forest land, deposition from aerial applications, and discharge of industrial waste etc., [3]. The wide range of pesticides and related compounds used makes it extremely difficult to develop a single method for pesticide disposal that applies universally. Therefore, various types of methods have been developed with respect to removal of specific class of pesticides. Various techniques like solvent extraction, chemical exchange membrane technology, reverse osmosis, filtration and adsorption are used for water treatment. Amongst the various treatment techniques mentioned above, adsorption is one of the effective method for lowering concentration of is extensively used for treatment of effluent containing pesticides and other related compounds. In spite of this it suffers from few disadvantages. Activated carbon is quite expensive and its regeneration produce additional effluent and considerable loss (10–15%) of the adsorbent [4]. In the recent years extensive research is going on in the field of surfactant based separation processes such as micellar chromatography, micellar-enhanced ultra filtration, and cloud point extraction, solubilization of organic compound by adsolubilization and by using organo-clays. Admicellar solubilization technique is based on the use of solubilization power of hydrophobic environment of surfactant aggregates formed at solid/liquid interface. Many organic compounds like phenols and substituted phenols have been removed. But work done on removal of herbicide is rare and scanty.

Metal oxide such as alumina possesses high surface area, but its surface is hydrophilic and has low adsorption affinity for organic compounds having low water solubility. Work [5,6] has shown that alumina can be modified by surfactant coating to enhance their sportive capacity towards organic compounds. The adsorption on metal oxide is pH sensitive [7]. Adsorption of surfactant on metal oxides occurs through coulombic attraction between charged alumina surface and the oppositely charged surfactant head group. Van der Waals forces between the long chains of surfactants lead to the formation of admicelles and hemimicelles on the surface [8]. The process of solubilization of organic compounds in hemimicelles and admicelles is termed as "adsolubilization" [6]. The process of adsorption of an anionic surfactant is greatly influenced by pH of the solution and, hence it is interesting to study contribution of solubilization power of the surfactant aggregates to enhance adsorption of low water soluble toxic pollutants and corresponding application in wastewater treatment.

EXPERIMENTAL PROCEDURE

Materials

The surfactant used was sodium sulfate (SS), of 99% purity. The alumina used had a surface area of $155 m^2/g$ and it was obtained from S.D. Fine Chemical Company. The properties of alumina and surfactant are given in Table 1. Herbicide used in the experiment is imedazoline. Information about imedazoline is given in Table 2.

Methods

Adsorption equilibrium study

Batch experiments were performed in Erlenmeyer flasks of total volume 250 ml. The final aqueous volume in each of the flask was 50 ml. Each solution contained 1.0 g of alumina and prescribed amount of 1M NaOH and S.S solution. The pH was adjusted using 1M hydrochloric acid and/or 1M sodium hydroxide. The flasks were capped and equilibrated for 24 h on orbital shaker, and then supernatant solution was analyzed for S.S using the classical methylene blue assay method [9]. The amount adsorbed onto alumina was determined spectrophotometrically using Shimadzo UV–vis spectrophotometer. The concentration of the imedazoline in each solution was determined spectrophotometrically using Shimadzo UV–vis spectrophotometer. All measurements were made at the wavelength corresponding to maximum absorbance (λ_{max}) of imedazoline .All the equilibrium study is carried out at the pH=6 and temperature of the solution is 30 ± 2 °C.

Adsorption kinetic study

The kinetic study were carried out in a glass jacketed baffled vessel. In each experiment 500 ml of aqueous solution of known concentration was taken in the vessel and stirred by using an eight bladed glass stirrer. A digital speed indicator monitored the speed of the stirrer. The temperature of the system was controlled ($\pm$ 2 °C) by means of thermostatic water bath in which the reactor vessel was immersed. Weighted amount of adsorbent was then added, and the kinetic measurements were reported. The kinetic of adsorption is studied at various predetermined time by withdrawing the required a liquor from the reactor vessel at suitable time intervals.

RESULTS AND DISCUSSION

Adsorption of S.S on Alumina

Fig. 1 shows the S-shaped isotherm for the adsorption of an anionic surfactant, S.S on alumina. The adsorption is carried out at pH=6. The adsorption is a strong function of pH. There is an increase in surface potential with decreasing pH. Therefore, negatively charged S.S surfactant ions are adsorbed at low pH values due to increased interactions between the alumina and S.S [10]. At low surfactant concentration coulombic interactions are the primary forces responsible for adsorption. As adsorbed concentration increases to a certain value, S.S molecules aggregates on the alumina surface through van der Waals interactions between the long hydrocarbon chains of the surfactant molecules.

These surface aggregates are called hemi-micelles. The concentration at which they are formed is called as hemimicellar concentration (HMC).

It is to be noted that the concentration of the surfactant in the aqueous phase is well below the CMC this indicates that there are no micellar species in the aqueous phase and the added surfactants exist as monomeric species. The hemi-micelle formation occurs at aqueous surfactant concentration that is approximately two orders of magnitude smaller than the CMC of S.S. As the S.S concentration in the aqueous phase increased further, bilayer of surfactant called admicelles are formed, there structures are characterized by a hydrophilic exterior and a hydrophobic interior. Further increase in aqueous surfactant concentration dose not increases the adsorbed concentration and a plateau is observed. The plateau in the surface adsorption of S.S is due to the fact that at these concentrations, the repulsive interactions between the head groups of surfactant are unfavorable to further adsorption of S.S [11].

Adsorption of imedazoline on alumina with and without S.S

Fig. 2 shows the adsorption isotherms of imedazoline with and without S.S on alumina. The adsorption of imedazoline on alumina in the absence of any S.S in the solution was seen to be less, but considerable enhancement in adsorption of imedazoline is observed in presence of SDS on alumina. From this figure, it can be seen that the nature of adsorption isotherm follows L type of Giles classification [12]. Under this condition the adsorption of imedazoline on untreated alumina may be attributed to weak on surfactant treated alumina surface is primarily driven by hydrophobic exclusion of the molecule from the aqueous phase [6]. The adsorption of imedazoline on S.S coated alumina was fitted to Freundlich Isotherm equation. Fig. 3 shows the Freundlich Isotherms of adsorption of imedazoline on alumina and S.S treated alumina.

Freundlich Isotherm equation

Freundlich Isotherm equation is a widely used as empirical equation for adsorption study and is given by Eq. (1) as follows:

$$\ln q_e = \ln K_f + (1/n) \ln C_e \qquad \text{.............................}(1)$$

Where:

C_e = equilibrium concentration,

q_e = amount adsorbed at equilibrium,

n and K_f are constants for given adsorbate–adsorbent system.

A plot of ln *q*e versus ln*C*e would give the value of n and K_f . Fig. 3 shows Freundlich Isotherm for adsorbent/adsorbate systems, From Fig. 3 it was seen that the adsorption of imedazoline on alumina and S.S treated alumina obey Freundlich Isotherm equation, which suggest that the concentration of imedazoline on the adsorbent increases with increase in imedazoline concentration. The values of Freundlich constant are listed in Table 3.The value of K_f can be used as alternative measure of adsorption capacity, while 1/n determines the adsorption intensity. The value of the Freundlich constant K_f for adsorption of imedazoline by S.S treated alumina revealed that the behavior of imedazoline in alumina–water system with micelle forming surfactant mainly depends on the degree of hydrophobicity of imedazoline [13].

Effect of pH

The effect of pH on adsorption by alumina or S.S treated alumina were studied by changing the pH of the solution from 2 to 11 and the results are shown in Fig. 4. In S.S treated alumina, adsorption decreases as the pH increases from 2 to 11. As pH decreases below 8.5 on alumina surface positive charge on alumina surface increases and amount of surfactant adsorbed is also increases. It has been reported that in case of adsorption of S.S on alumina surface, aqueous concentration at which hemi-micelles are formed i.e. HMC decreases as the pH decreases from higher to lower range. It has been also reported that at lower pH amount of S.S adsorbed concentration is much greater than at very high pH [14]. This may leads to considerable amount of solubilization of imedazoline in S.S aggregates formed at solid/liquid interface at lower pH value. Adsorption of imedazoline is mainly due to surfactant adsorption because a positively charged oxide surface with an adsorbed anionic surfactant layer on its surface, called organo oxide, act as an adsorbent for organic compounds [15]. As the pH increases gradual decrease in adsorption occur with respect to change in pH. This may be attributed by the increase in HMC with increase in pH. Therefore, the extent of imedazoline solubilized in surfactant aggregates at solid/liquid interface decreases and corresponding decrease in adsorption at higher pH value is observed. In absence of S.S, it is observed that the adsorption of Isoproturon increases with increase in pH from 2 to 8.5.

Above pH 8.5 adsorption decreases with increase in pH. Increase in adsorption of imedazoline with respect to increase in pH. At higher pH i.e. pH 9, decrease in adsorption with respect to pH may be attributed due to repulsion between negative charge developed on nitrogen of imedazoline molecule and negatively charged alumina surface (AlO^-). The effect of pH on adsorption of imedazoline on treated and untreated alumina clearly showed the role played by electrostatic interaction and extent of solubilization by surfactant at solid/liquid interface.

Pseudo-second order kinetics

The sorption kinetics may be described by the pseudo second order model, which is shown in following equation. The pseudo-Second order rate equation of 'Ho' [16] has been successfully applied to the sorption systems such as those of basic and acid dyes on peat [17].

$$dq_t/dt = k(q_e-qt)^2 \qquad \ldots\ldots(2)$$

$$1/(q_e-q_t) = (1/q_e) + kt \qquad \ldots\ldots(3)$$

Equation (2) can be rearranged to linear form:

$$t/q_t = (1/kq_e^2) + (1/q_e)t \qquad \ldots\ldots(4)$$

$$h= kq_e^2 \qquad \ldots\ldots(5)$$

q_e = is the amount of imedazoline molecule adsorbed at equilibrium (mg/g); q_t = is the amount of imedazoline molecules on the adsorbent at any time 't' (mg/g).

The product k_1qe^2 is actually the initial sorption rate represented as $h = kqe^2$ where k is rate constant. The straight line plots of t/q_t versus t at different concentrations, agitation speeds, mass of adsorbents and temperatures suggest the applicability of Ho and McKay equation to the present system and also explain that the process of adsorption follows pesudo-second order kinetics. The values of k, h, and q_e were calculated from the slope and intercept of the plots.

Effect of mass of adsorbent

Effect of mass of adsorbent on adsorption of imedazoline on S.S treated alumina was studied by changing the mass of adsorbent from 0.5 to 1.5 g and the results are shown in Fig. 5. From this study it can be observed that with increase in adsorbent mass, amount adsorbed per gram decreases. Kinetic data of adsorption of imedazoline on S.S treated alumina follows the pseudo-second order rate expression with the regression coefficients for the linear plots being higher than 0.99. From Table 4, it can be seen that the equilibrium adsorption capacity decreases from 19.15 to 16.18 mg/g for S.S treated alumina as the mass of adsorbent varies from 0.5-1.5 gm.

CONCLUSIONS

1. An alumina surface changes its characteristics from hydrophilic to hydrophobic upon adsorption of an anionic surfactant (S.S) at pH less 8.2.

2. The surfactant treated alumina is found to have greater adsorption capacity for imedazoline than untreated alumina.

3. Regrational analysis showed that experimental data fitted in Frendulich Isotherm.

4. Adsorption process for adsorbate/adsorbent system is found to be pseudo-second order.

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Table (1) Properties of adsorbent and surfactant

Adsorbent	Alumina
Surface area	$155 m^2/g$
Point of zero charge	8.5
Surfactant	Sodium sulfate
Molecular weight	288.8
Critical miceller concentration	0.008M

Table 2 Properties of imedazoline

Adsorbent	Alumina
Herbicide	imedazoline
Molecular weight	206.29
Molecular formula	$C_{12}H_{18}N_2O$
Water solubility	60 mg/l

Table 3 Freundlich constants for adsorption of imedazoline

Adsorbent	K_f	1/n	R^2
Alumina	4.25	6.329	0.8001
Alumina modified with S..S	3.443	0.6952	0.9709

Table (4) Second order kinetic constants for adsorption of Isoproturon on S.S treated alumina at different mass of adsorbents

Mass of adsorbent (gm)	q_e (mg/gm)	h (mg/gm.min)	K (mg/gm.min)	R^2
0.5	19.15	7.456	0.02031	0.9991
1.0	17.73	5.227	0.01662	0.9965
1.5	16.18	3.471	0.1325	0.9933

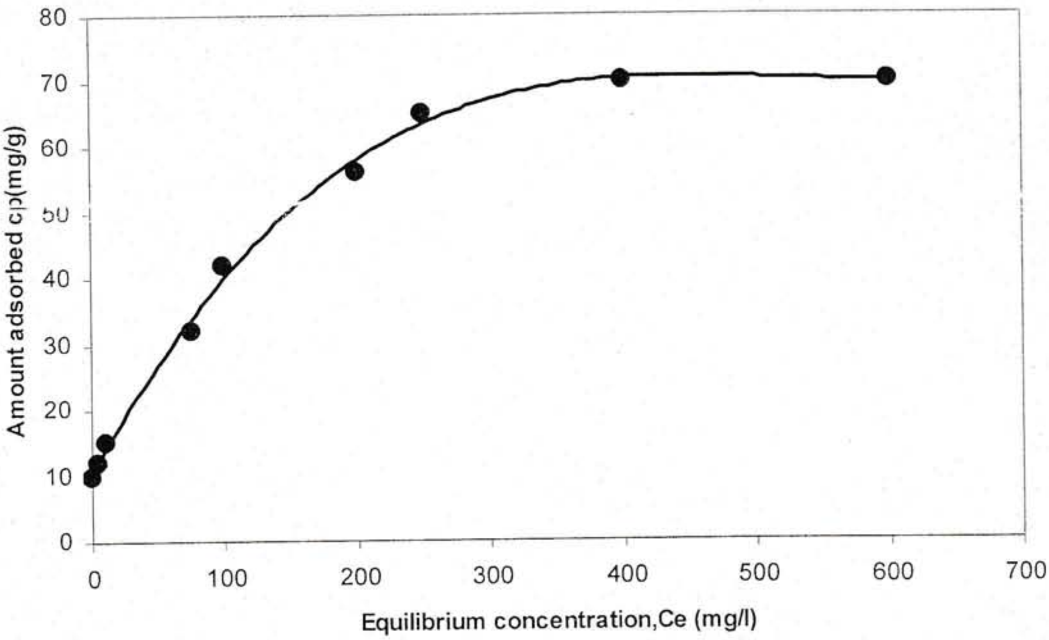

Fig. 1. Adsorption isotherm of S.S on alumina.

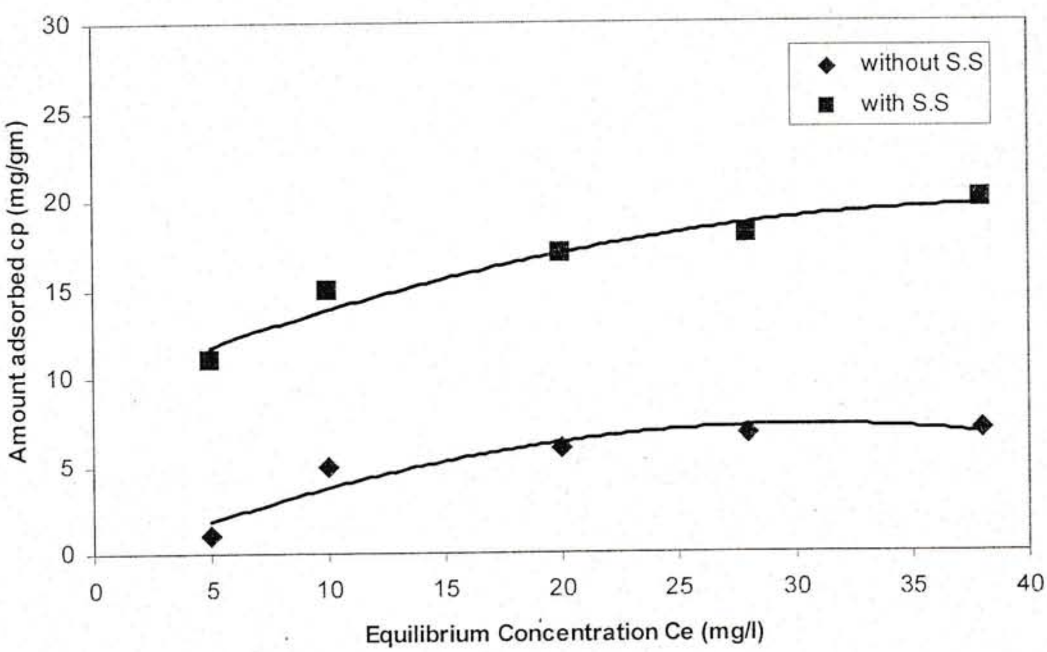

Fig. 2. Adsorption isotherm of imidazoline on alumina.with and without S.S

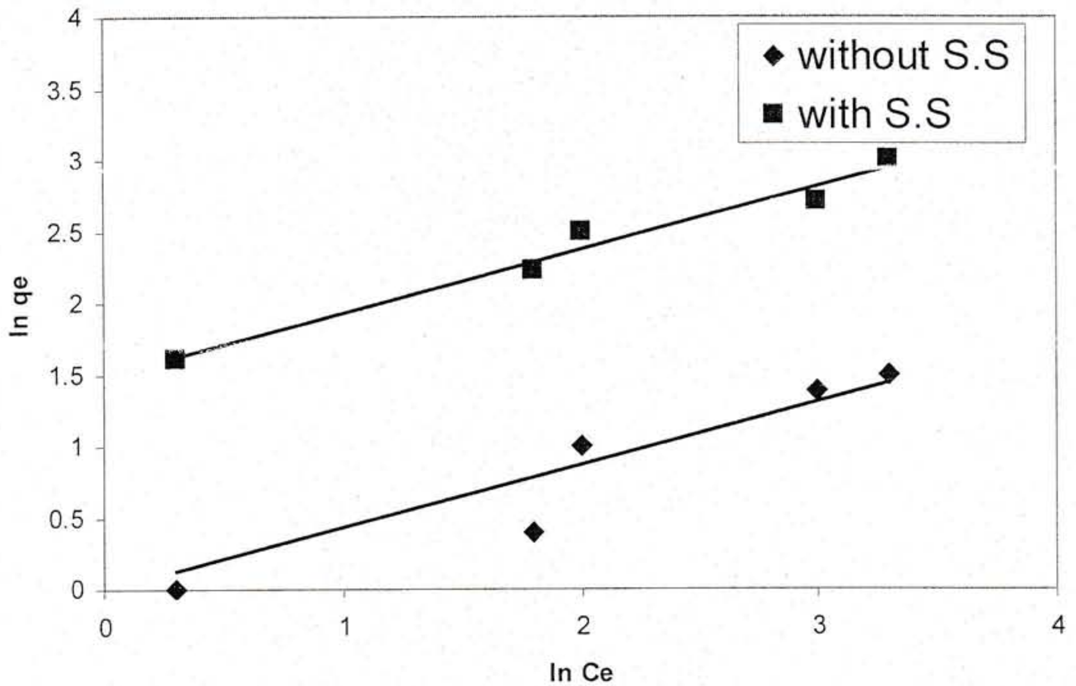

Fig. 3. Freundlich Isotherms for the adsorption of Imidazoline on alumina with and without S.S.

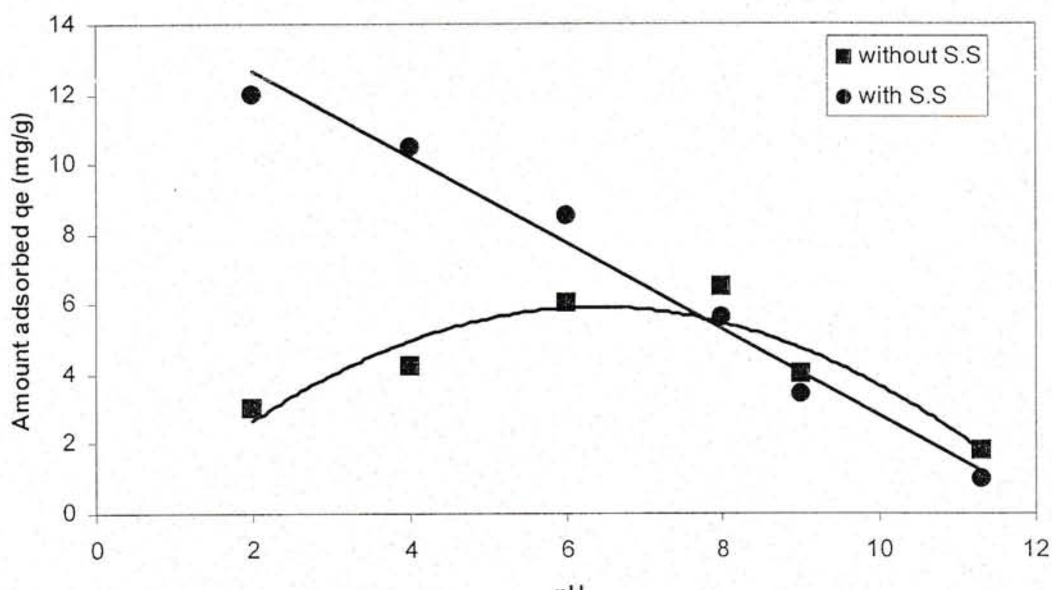

Fig. 4. Freundlich Isotherms for the adsorption of Imidazoline on alumina with and without S.S.

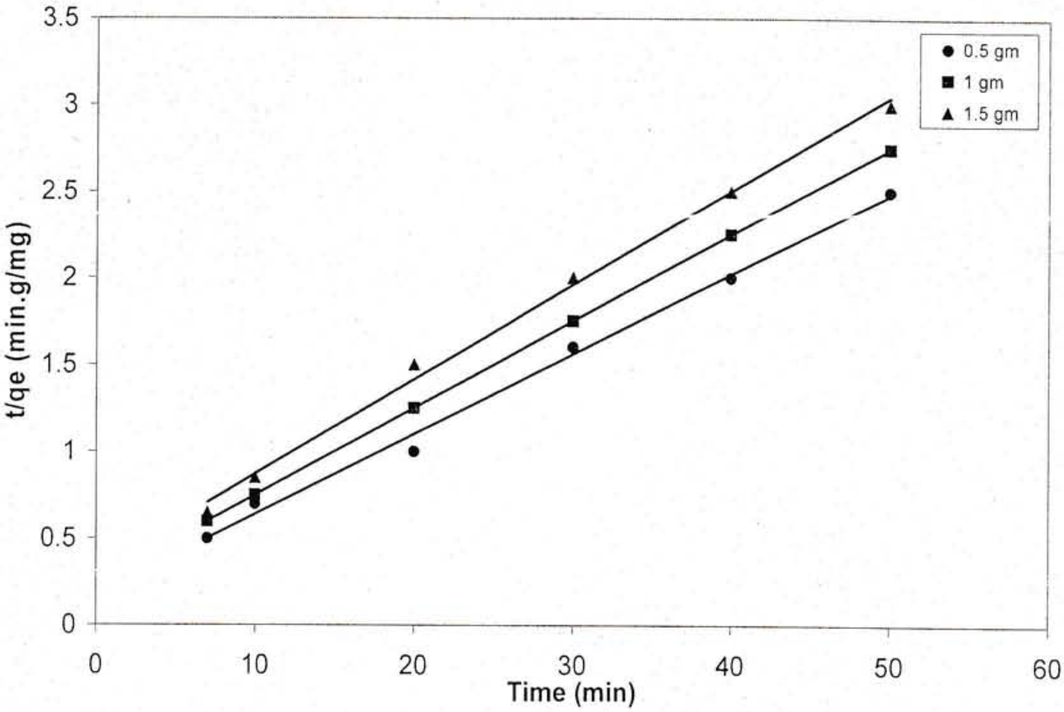

Fig. 5. Pseudo-second order kinetic plot for the adsorption of Isoproturon on surfactant treated alumina at different mass of adsorbents.

معالجة مياه الفضلات باستخدام الألومينا المحسنة

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الخلاصة

تم تحسين امتزاز سطح الألومينا بواسطة امدصاص مواد منشطة للسطح و هي كبريتات الصوديوم ، تم الحصول علة ايزوثيرم بشكل حرف S بعد استخدام هذا المنشط.تمت دراسة كفاءة امتزاز الالومينا و الالومينا المعامل سطحها بالمادة المنشطة. لوحظ وجود تداخل في امدصاص الهيربسايد على السطح المعامل بالألومينا و الذي يمكن أن يساهم في ذوبانيته على سطح ذرات المنشط المتكونة عند السطح البيني للصلب/سائل. تمت دراسة تاثير الدالة الحامضية على الامدصاص ، و وجد أن الامدصاص ياثر بشكل كبير بالدالة الحامضية للوسط. و قد تمت دراسة مدى انطباق معادلة فريندلش على النتائج المستحصلة في حالة التوزان. و كذلك تأثير عدة عوامل مثل التركيز و وزن المادة المادصة. و تم اختبار حركية النظام على أساس أنه تفاعل من الدرجة الثانية ظاهريا و تم حساب ثوابت معدل التفاعل.

الكلمات الدالة

مياه الفضلات، مواد منشطة للسطوح، ألومينا