Elimination of isobutyl phenyl propionic acid (Ibuprofen) from wastewater by treated silica gel

Fouzia Belaib[1] ; Abdeslam-Hassen Meniai
1 : Laboratoire de l'ingénierie des procédés de l'environnement, Faculté de Génie des Procédés,
2 : Université Constantine 3, Constantine, Alegria, email : belaibfouzia@yahoo.fr

Abstract
The present study deals with the adsorption capabilities of treated silica gel to remove various pharmaceutical compounds from aqueous solutions, like the Isobutylphenylpropionic known as Ibuprofen (IBU) which is an anti-inflammatory drug widely used as antipyretics and analgesics.
In fact, this study showed that Silicagel coated was efficient for the elimination of ibuprofen. The effects of several operating parameters like contacting time, pH and temperature, were also investigated and discussed.
The obtained results showed that the highest sorption of ibuprofen onto the considered sorbent took place at low pH values. Also, the addition of KCl amounts into the solutions increased the sorbent retention capacity of IBU at ambient temperature of 20°C.

Keywords: *Adsorption; Ibuprofen; Kinetic; Non-steroidal anti-inflammatory; Silica gel —*

I. Introduction

Many industrial wastewater effluents contain pharmaceutical pollutants which do have an environmental impact and may cause possible damages to botany and fauna present in aquatic systems (Ternes et al., 2004). One of mostly consumed medicines corresponds to the classification of the Non- Steroidal Anti-Inflammatory Drugs (NSAIDs) with more than 70 million annual prescriptions in the world**.** For instance, several recent reports have confirmed the presence of the NSAID Ibuprofen (IBU) in effluents of wastewater treatment plants (WTPs) at concentrations ranging between 10 and 169 mg L^{-1} (Santos et al., 2007).

The removal of IBU from aqueous phases using different supports has been reported in the literature where it has been clearly shown that high costs and difficulties in regeneration of these supports have encouraged researchers to look for new sorbents (Gurses et al. 2004). One can cite the example of Silicagel treatment with suitably chosen polymer, showing several advantages over other commercial-grade adsorbents such as a high adsorption capacity to eliminate different kind of pollutants. However, this property may be influenced by certain operating parameters such as the solution pH which may affect the presence of surface functional groups in IBU molecule and in the sorbents, hence influencing the sorption properties of ibuprofen**.**

Therefore the aim of this work is to investigate the efficiency of alternative Silica gel treated with polymer for the removal of ibuprofen from wastewaters.

II. Materials and methods

A commercial porous silica gel supplied by PROLABO as spherical particles with diameters ranging from 63 to 200 µm, specific area of 500 m^2/g and a porous volume of 75 cm^3/g. In order to eliminate any possible impurities, a washing with Hydrochloric acid was performed and followed by a rinsing with distilled water and a drying before storage in a desiccator.

The treatment of the dried Silicagel support consisted of a polyaniline coating by means of an in situ polymerization which was carried out according to the following steps:

- Introduction of Aniline (supplied 99.8% pure by ACROS ORGANICS, France) just after a distillation, into a sealed beaker containing, a priori, Ammonium persulphate (supplied by LABOSI, France);

- A continuous stirring of the mixture (Aniline, Ammonium persulphate and Silicagel) for about 2h;
- Filtration and washing with Hydrochloric acid of the obtained product;
- Drying of the product at 95°C in a furnace and obtention of a fine powder of a green color confirming the surface deposition of Polyaniline as reported in the literature [Uvdal et al].

The Ibuprofen adsorbate was 99% pure and was supplied by Sigma-Aldrich. Table 1 illustrates its different physico-chemical properties are shown in Figure 1 as follows:

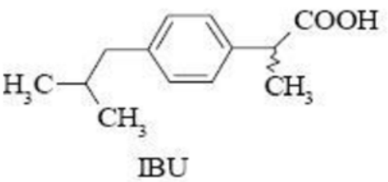


Figure 1. Molecular structure of ibuprofen.

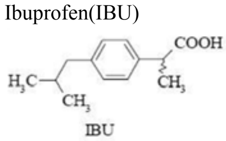
Solutions were prepared by dissolving 8mg of Ibuprofen in 1000 ml of distilled water. A priori, all the glassware was rinsed and washed using acid and distilled water. A mass of 30mg of Silicagel and 30 ml of ibuprofen solution were mixed in an Erlen Meyer and then agitated. The separation was carried out by filtration and the dosage of the filtered solution was performed by means of UV-vis Spectroscopy using a Shimadzu UV-160A spectrophotometer.

The adsorption amount q of the molecules at the equilibrium step was determined according to the following equation:

$$q = \frac{(C_0 - C)}{r} \text{ V} \qquad (1)$$

where q is the adsorption capacity (mg agent/g adsorbent), C_0 and C are the initial and final adsorbate concentrations, respectively in (mg/l), m the mass of adsorbent (g), V the volume of the solution (l) and r the solid to liquid ratio (g/l).

Table 1: Physico-chemical properties of ibuprofen

Compound	Molar weight (g.mol^{-1})	Water solubility (25 °C) (mg.dm^{-3})	Log Kow
Ibuprofen(IBU) 	206.28	21	4.13-4.91

III. Results and discussion

1. Effect of contact time

Figure 2 shows the effect of the contact time on the retention capacity of ibuprofen onto the solid support. A very rapid step was shown just at the beginning where the retention capacity increased sharply due the great availability of vacant sites at the adsorbent surface, and then practically, after 15 min, it remained constant with time, assuming that equilibrium was reached.

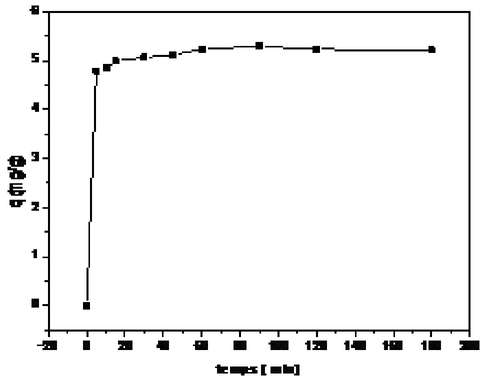


Figure 2. Effect of contact time in the IBU retention onto silica gel (Experimental Conditions: C_0=8mg/l, v=600 rpm, T=22°C, r=10g/l, pH≈6.8)

2. Effect of initial concentration

The results also showed that that the amount of adsorbed ibuprofen increased with an increase of the initial drug concentration. The effect of the variation of the ibuprofen concentration was important on the retention process. In order to study its effect, concentration values of 4, 8, 12, 16 and 20mg/l were considered. The results obtained are shown in Figure 2 and one can see that the retention process was really influenced by the initial concentration of the drug in the solution. In fact the elevation of the latter generated a rise in the adsorbed amount of the pollutant, while there were free sites on the surface of the adsorbent, the adsorption capacity (retention) increased up to the saturation of these sites.

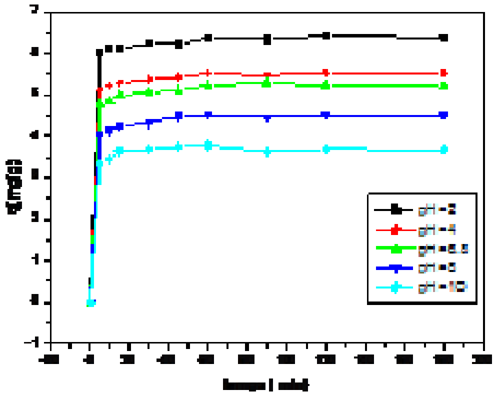


Figure3. Effect of initial concentration of IBU retention onto Silicagel treated (v=600 rpm, T=22°C, r=10g/l, pH≈6.8)

3. Effect of pH on adsorption

The effect of initial pH was investigated at various values ranging between from 2 to 10 and the results are shown in figure 4. In terms of removal efficiency, 79.88% was reached at pH = 2 and decreased to 46% at pH= 10.

Changes in pH affected the dissociation of the ibuprofen molecule where, according to the dissociation constant of ibuprofen molecule, (pKa = 4.91), more than 50% of the drug compound was expected to be deprotonated. Generally, an increase in the solution pH results in partially or fully deprotonated surface functional groups and thus a loss of positive charge and/or a negative charge build up (Wang et al. 2007). When the sorption occurred above pH = 9 the anionic form of ibuprofen was dominant in solution . From practical application point of view, Silicagel treated with polyaniline, seemed to have good potential to remove higher amounts of ibuprofen from water at acidic pH.

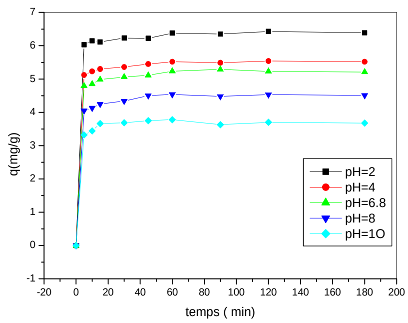


Figure 4: Effect of solution pH on ibuprofen sorption capacity, (Conditions : C_0=8mg/l, V=600rpm, T=22°C, r=10g/l)

4. Effect of ionic strength on ibuprofen sorption

The effect of salt nature on the removal percentage of ibuprofen is important. Different salts, namely NaCl, KCl and $CaCl_2$ were considered. The results are presented in figure 5 and show that the addition of KCl had a great effect on the retention of IBU. Such behavior was anticipated due to an interaction between the surface and added solutes which may block some of the adsorption active sites for ibuprofen molecules.

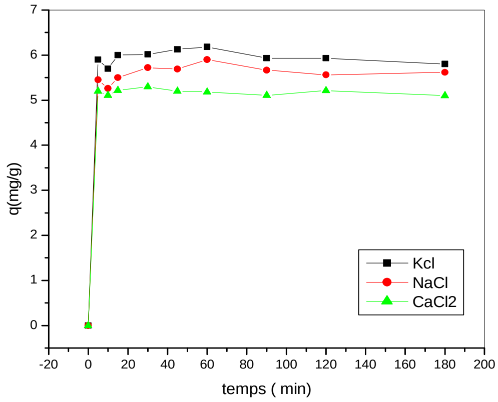


Figure 5: Effect of ionic strength on ibuprofen sorption capacity (Conditions: C_0=8mg/l, V=600rpm, T=22°C, r=10g/l)

5. Effect of temperature on ibuprofen sorption

The effect of temperature on the removal of IBU on treated silica gel treated was investigated at different temperature as shown in figure 6.The removal percentage of IBU decreased from 65.12 to 45%, when the solution temperature increased from 20 to 50°C. Since the adsorption decreased, when the temperature increased, the system was considered to be exothermic.

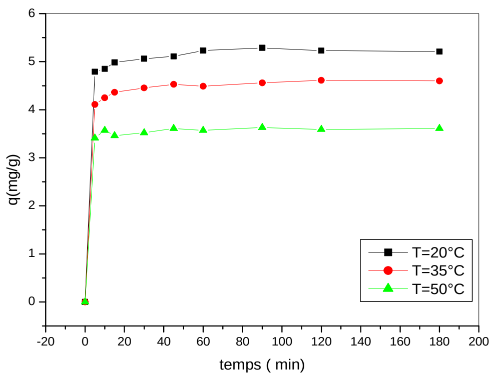


Figure 6: Effect of temperature on ibuprofen sorption capacity, (Conditions: C_0=8mg/l, V=600rpm, r=10g/l)

6. Thermodynamic study

The calculation of thermodynamic parameters is required for the study of the nature of the retention process and is performed by means of the following relationship:

$$lnK_D = \frac{lnQ_e}{C_e} - \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (1)$$

with R the universal gas constant (R ¼ 8.314 J/mol K), T the temperature (K), Kd the distribution coefficient, Qe the adsorbed quantity onto the solid (mg/g), Ce the concentration at equilibrium (mg/l), ΔH° the standard enthalpy (J/mol) and ΔS° the standard entropy (J/mol K).

The values of ΔH° and ΔS° were calculated from the slope and intercept of the plot of lnK_D versus 1/T and ΔG° can be calculated using the following relationship:

$$\Delta G^0 = -RTlnK_D \quad (2)$$

The results are shown in the following table:

Table3 : Thermodynamic parameters

Support	ΔH (kJ /mol)	ΔS (kJ/mol K)	ΔG (kJ/mol)		
			20 °C	35 °C	50 °C
Treated Silica gel	-0.007	-0.815	238.8	251.00	263.22

The positive values of ΔG° indicate that the adsorption process of ibuprofen is not spontaneous and that the retention process is a chimisorption. The negative values of ΔH° indicates that the nature of the reaction is exothermic and is expressed by the reduction of the amount adsorbed of ibuprofen with increasing temperature and the positive value of ΔS° with the support indicates increasing randomness at the solide-solution interface.

7. Adsorption kinetics study

A kinetic study was performed by testing two kinetic models for the obtained experimental data as follows:

a. Pseudo-first-order model: it is described by the following equation:

$$log(q_e - q_t) = log(q_e) - k_1 t/2.303 \quad (3)$$

where q_e and q_t refer to the amount of ibuprofen adsorbed (mg g^{-1}) at equilibrium and at any time, t (min), respectively and k_1 is the equilibrium rate constant of pseudo first-order adsorption (min^{-1}).

b. Pseudo-second-order model: it is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where k2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). Experimental kinetic data were adjusted according to the indicated models. Table 2 showed that the second order equation model provided the best correlation with experimental results. This fact indicates that the sorption of ibuprofen on adsorbent followed the pseudo-second order kinetics.

Table2: The correlation factors and the kinetics constants of the two kinetic models of IBU

Model	First order kinetic		Second order kinetic	
Support	k_1	R^2	k_2	R^2
Silica gel	0.01329	0,93385	1.1655	0.99999

8. Adsorption isotherm

In order to optimize the design of adsorption system of the ibuprofen removal, it was important to establish the most appropriate correlation for the equilibrium curves .These equilibrium adsorption capacity curves can be obtained by measuring the adsorption isotherm of ibuprofen onto adsorbent. Different models of sorption isotherms including Langmuir, Freundlich and BET were tested in the present study, as shown in Table 4. Q_e is the equilibrium sorbate concentration on the sorbent, Q_{max} is the maximum adsorption capacity, K_L is Langmuir constant. K_F is Freundlich constant related to the sorption capacity, n is the heterogeneity factor and K_{BET} is BET constant

A model can be considered the most suitable to satisfactorily describe the sorption process if it provides the highest R^2. Consequently the high R^2 (0.995) for the BET model indicates that the adsorption of ibuprofen onto treated Silicagel followed the BET model, confirming that the adsorption was of multilayers.

Table 4: Isotherm constants of the three models

Model	Linear form	constants	Support Treated Silica gel
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{1}{Q_m K_L}$	Q_m	-5.7943
		K_L	1.09826
		R^2	0.99114
Freundlich	$lnq = lnK_F + \frac{1}{n} lnC_e$	K_F	6.84535
		n_f	-6.36375
		R^2	0.9793
BET	$\frac{C_e}{q_e(C_0 - C_e)} = \frac{1}{q_m \cdot K_{BET}} + \frac{K_{BET} - 1}{q_m \cdot K}\left[\frac{C_e}{C_0}\right]$	K_{BET}	0.79337
		q_m	1.75334
		R^2	0.99544

IV. Conclusion

The removal of ibuprofen from the aqueous solutions through treated Silicagel was considered. The effect of key operating parameters such as the initial pH, the initial drug concentration, the ionic strength and the temperature, on the adsorption capacity was investigated. The adsorption kinetic study of ibuprofen onto Silicagel showed that the process followed a pseudo second order rate.The thermodynamic study confirmed that the retention process was based on chimisorption and that it was not spontaneous with the adsorption of ibuprofen following the BET model.

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