Removal of ibuprofen from water using recycled clay waste

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Received:11 May 2023; Accepted: 02 August 2023; Published: 30 August 2023

Abstract

This work presents studies on the regeneration of spent bleaching earth (SBE) from edible oil refinery and the use of recycled material (RSBE) in the treatment of water containing ibuprofen. This waste is bentonite (clay) that is activated by sulfuric acid at hot and used to bleach edible oils. The regeneration method used in this study was thermal treatment of clay waste (SBE) in a furnace at 400 °C for 1 h, followed by cold washing with 1 M hydrochloric acid solution. Recycled material (RSBE) is characterized by a variety of techniques (X-ray diffraction, FTIR and fundamental methods). The characterization results showed that the bentonite structure was not affected by the heat treatment and that the treatment only resulted in the disappearance of organic compounds from the spent bleaching earth. Subsequently, regenerated spent clay (RSBE) was tested for the removal of ibuprofen from aqueous solutions by adsorption to estimate the efficiency of the regeneration method used in this study. The effects of physicochemical parameters on the ibuprofen adsorption by regenerated spent bleaching earth and virgin bleaching earth (VBE) were focused. The obtained results indicated that ibuprofen was rapidly adsorbed onto both materials. The amount of ibuprofen adsorbed on the both adsorbents increased with the increase of the initial solute concentration. The pH value of the solution plays a very important role in the ibuprofen adsorption by the recycled waste (RSBE). The elimination of ibuprofen is maximized in an acidic environment. Kinetic modeling showed that the second-order kinetic pseudo-model could well describe the adsorption process. The adsorption isotherms followed the Langmuir and Freundlich model. Calculation of q_{max} and 1/n with these two isotherms indicated that the recycled material had found its adsorption capacity and could be used as an inexpensive sorbent for the removal of ibuprofen.

Keywords: Spent bleaching earth, Waste, Regeneration, Ibuprofen, Adsorption.

Tob Regul Sci. ™ 2023;9(1): 4793-4804

DOI: doi.org/10.18001/TRS.9.1.334

1. Introduction

Water is the main constituent of beings living and an essential element for all life forms. Its availability and abundance play a fundamental role in the growth and development of society. The water pollution by some chemicals of industrial origin (hydrocarbons, phenols, dyes, drugs...) or agricultural origin (pesticides, fertilizers...) are a source of environmental degradation and a major problem facing the authorities and the international community. Drugs are among the many chemicals that can contaminate aquatic and terrestrial environments. These are synthetic or natural compounds used in human or veterinary medicine. They contain active ingredients conceived to have a pharmacological and therapeutic effect. Every year, thousands of tons of drugs are used to treat symptoms, diseases and bacterial infections. However, residues of these substances are transferred in various ways into the aquatic environment and have been detected, in some cases, in drinking water (Reemtsma et al., 2006; Glassmeyer et al., 2008; Verlicchi et al., 2012).

In recent years, more than 150 pharmaceutical products of different therapeutic classes have been detected in different environmental matrices (Heberer, 2002). Pharmaceutical products detected in water ibuprofen. It is a non-steroidal anti-inflammatory drug, analgesic, and antipyretic widely used in the treatment of rheumatism (Mestre et al., 2007). Due to its ability to bypass traditional wastewater treatment, it has not been completely eliminated. In this context, adsorption is one of the proven methods to recover micropollutants from aqueous solutions.

The aim of this study is to remove ibuprofen by adsorption using regenerated spent bleaching earth (RSBE). The material is obtained by recycling spent bleaching earth (SBE) from edible oil refinery. SBE is the solid waste or filter cake obtained at the end of the bleaching edible oils operation. After this step, this waste contains impurities (oxidation products, heavy metals, soaps, phospholipids, adsorbed dyes...) but also large quantities of oils that remain from the various refining stages. For ecological and environmental reasons, the authorities prohibit the discharge of such waste, as these pollutants not only present a risk of spontaneous combustion, but are also a potential source of water pollution and produce unpleasant odours. Spent bleaching earth is classified as hazardous waste according to the European Waste Catalogue, with code 07 06 10* (Rehab et al., 2014). In view of the various environmental problems arising from the disposal of spent bleaching earth, regeneration of this waste is of vital importance.Given these different environmental problems caused by discarding spent bleaching earths, the regeneration of this waste is paramount. The regeneration method used in this study focuses on a furnace heat treatment at 400 °C followed by a cold wash with standard hydrochloric acid solution. The recycled material (RSBE) is then used in the treatment of waters containing ibuprofen.

2. Materials and methods

2.1. Materials

The virgin bleaching earth (VBE) and the spent bleaching earth (SBE) used in this study were provided by the unit of edible oil refining COGB-Label of Bejaia (Algeria). The VBE is a bentonite coming from Maghnia deposit (Algeria), activated at hot with sulfuric acid and marketed by BENTAL Company. The major chemical components of this material are as follows: 61.96 % SiO_2, 1.59 % MgO, 9.81 % Al_2O_3, 0.01 % K_2O, 2.92 % CaO, 3.51 % Fe_2O_3, and 0.05 % Na_2O. The pharmaceutical compound used in the present study is ibuprofen ($C_{13}H_{18}O_2$, MW = 206.28 g mol^{-1}, λ_{max} = 228 nm). It molecular structure is depicted in Figure 1. This compound was provided us by the SAIDAL Company of Algiers.

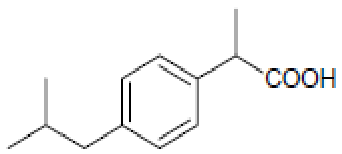

Figure 1: Molecular structure of ibuprofen.

2.2. Regeneration of the Spent bleaching earth

A complete description of the SBE regeneration method can be found in a previous study (Boukerroui et al., 2018; Aberkane et al., 2021). An amount of spent bleaching earth (SBE) is placed in porcelain crucibles and heat-treated in a muffle furnace (Nabertherm D-2804) for 1 hour at 400 ° C. After the heat treatment, the obtained material is washed with a normal hydrochloric acid solution (5% (w/w)) at room temperature for 1 h. The sample leached with HCl solution is then filtered and washed repeatedly with distilled water until negative test with $AgNO_3$. The regenerated spent bleaching earth (RSBE) thus obtained is dried, crushed, sieved and kept free from contamination.

2.3. Characterization of materials

The DRX spectra of the materials (VBE, SBE and RSBE) have been obtained with monochromatic CuKα radiation using an X Pert Pro Panalytical diffractometer. The FTIR spectra of different samples were carried out with SHIMADZU FTRI 8400, in the range 4000–400 cm^{-1} (lozenge of KBr 1%). The point of zero charge (pH_{PZC}) of the samples was determined. It corresponds to the solution pH for which the net surface charge of the solid is zero. For the experimental protocol, 50 ml of aliquot of 0.01 M NaCl solution are prepared in several erlens. Their pH is adjusted by means NaOH or HCl. Once the constant pH, 0.15 g of the adsorbent is added in each erlen. These are sealed and stirred for 24 h. The filtrates are recovered and their pH is measured. The pH_{PZC} corresponds to the point where pH_i = pH_f (Guo and Rockstraw, 2007).

2.4. Ibuprofen removal

The influence of some parameters on the adsorption process of ibuprofen on both adsorbents was presented. The parameters studied are: the initial concentration of ibuprofen, the contact time and the initial pH. To study the effect of the initial concentration of ibuprofen (20, 40 and 60 mg L^{-1}) on adsorption kinetics, 30 mL of Ibuprofen solution were mixed with 20 mg of the adsorbent (RSBE) After a given stirring time, the suspensions were filtered and the ibuprofen concentrations in the supernatant were measured with UV-visible spectrophotometer (SHIMADZU UV-1800) at 228 nm wavelength.

The amount of ibuprofen per unit mass of adsorbent at time t, q_t (mg g^{-1}), was then determined by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Where C_0 and C_t (mg L^{-1}) are the initial concentration and liquid phase concentration of the ibuprofen solution at time t (min), respectively, V (L) is the volume of aqueous solution containing ibuprofen, and m (g) is the mass of adsorbent used.

The influence of initial pH, at 25 °C, was studied over a pH range between 2 and 12. For this, HCl or NaOH were added to the ibuprofen solution to adjust the desired pH. The measurements were made in a pH meter.

The removal rate (R %) is defined as the efficiency of the adsorption reaction. This is the ratio of the ibuprofen amount at time t to that initially found in the aqueous solution. It was determined by the following equation:

$$R\,(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (2)$$

Where C_e is the liquid phase concentration of the ibuprofen solution at equilibrium.

3. Results and discussion

3.1 . Characterization

The FTIR spectrum of different samples VBE, SBE and RSBE (Figure 2) show the disappearance of the edible oil characteristic bands in the spent bleaching earth after the heat treatment (RSBE) at 400 °C. These bands are those corresponding to C-H stretching at 2925 and 2854 cm^{-1} and the ester carbonyl vibration at 1736 cm^{-1} [Meziti and Boukerroui, 2011; 2018). The departure of these compounds does not reveal any notable changes in the structure the bentonite. This result is confirmed by the X-ray diffraction (Figure 3) which shows that the crystalline structure of the bentonite is not affected by the heat treatment.

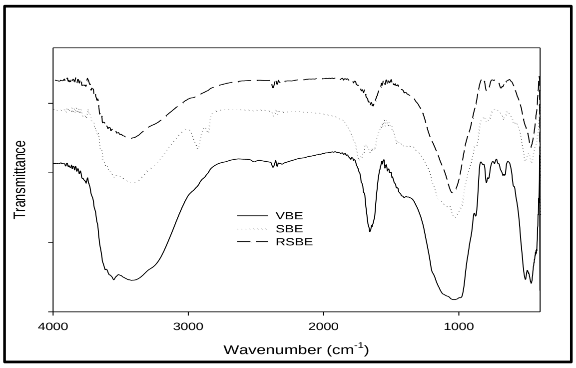

Figure 2: FTIR spectra of VBE, SBE and RSBE

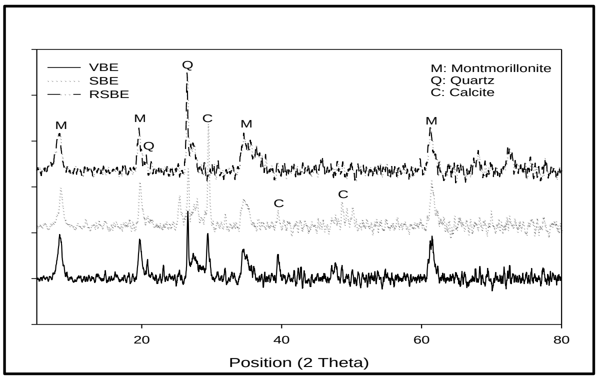

Figure 3: X-ray diffraction of VBE, SBE and RSBE

Figure 4 shows the graphical method used to determine the point of zero charge (pH_{PZC}) of the two materials VBE and RSBE. According to the graphs, the VBE has a pH_{PZC} of 7.7 versus 6.8 for the RSBE. This result means that the RSBE surface is more acidic than that of the VBE.

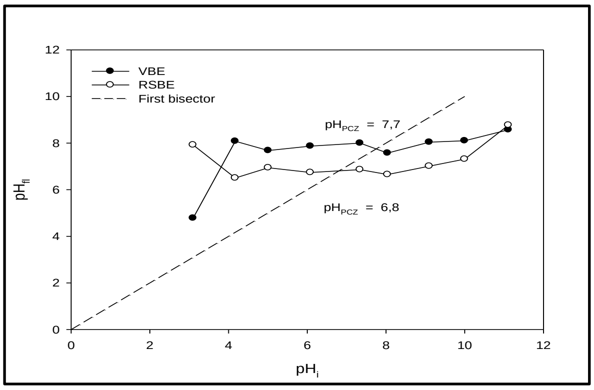

Figure 4: Determination of the point of zero charge (pH_{PZC}) of the both materials VBE and RSBE.

3.2. Adsorption Kinetics

After the regeneration of the material (RSBE) and its characterization, its adsorption capacities are tested in the removal of ibuprofen present in aqueous solution, by referring to the virgin bleaching earth (VBE). The curves of adsorption kinetics for different concentrations (20, 40 and

60 mg L^{-1}) were obtained by plotting the adsorption capacity q_t (mg g^{-1}) according to time (min). The evolution of the adsorption capacity as a function of time for VBE and RSBE is shown in Figure 5 and Figure 6, respectively. The obtained curves show that the adsorption rate of ibuprofen on the both materials evolves quickly in the first minutes of contact ibuprofen - adsorbent, followed by a slow increase until reaching equilibrium. The time necessary to reach this equilibrium was less than 30 min for the two materials. The fast adsorption kinetics, noted at the beginning of the process, can be interpreted by the fact that at this moment the number of active sites available on the surface of the material is important. After a while, the remaining vacant sites become difficult to access because of the existence of repulsive forces between the molecules of ibuprofen adsorbed by the material and those in solution (Lian et al., 2009).

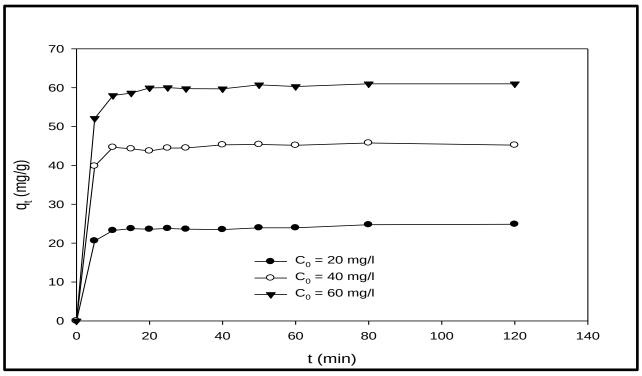

Figure 5: Kinetic results of ibuprofen adsorption on VBE for different concentrations

(pH = 4 ; m = 0.02 g ; V = 30 ml, w=300 rpm ; T = 25°C)

Figure 5 and Figure 6 show that the amount of adsorbed ibuprofen on the VBE is very close than that of RSBE for all concentrations. The shape of the curves shows that the increase in the initial concentration of the solute leads to an increase in the amount of ibuprofen adsorbed for the two adsorbents. This is due to the presence of a strong solute concentration gradient between the solution and the solid surface (Meziti and Boukerroui, 2012).

Several kinetic models are available to understand the behavior of the adsorbent and to predict the mechanism involved in the sorption process. The Lagergren's first-order kinetic model and the Ho's pseudo-second-order model are the most frequently used in the literature (Ho et al., 2000).

The pseudo-second-order model can be expressed by the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Integrating this equation for the boundary conditions t = 0 to t = t and q = 0 to q = q_t, gives:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

Where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed at time t (mg/g) and k_1 is the rate constant of pseudo first order adsorption (min^{-1}).

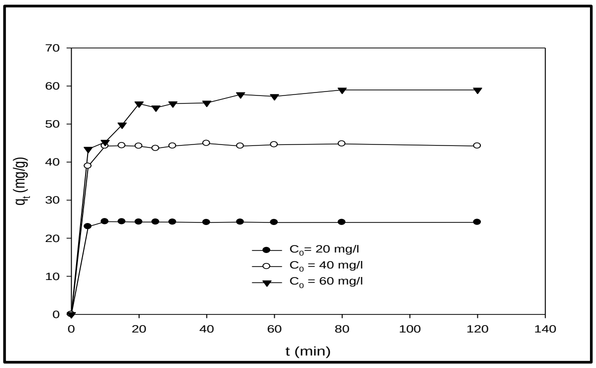

Figure 6: Kinetic results of ibuprofen adsorption on RSBE for different concentrations.

(pH = 4 ; m = 0.02 g ; V = 30 ml, w=300 rpm ; T = 25°C)

The validity of this model can be checked by linearized plot of ln (q_e – q_t) versus t. the rate constant of pseudo first order adsorption is determined from the slope of the plot.

The pseudo second order kinetic equation based on the adsorption capacity may be expressed in the form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5)$$

Where k_2 is the rate constant of pseudo second order adsorption (g/mg min).

Integrating the equation (5) for the boundary conditions t = 0 to t = t and q = 0 to q = q_t, gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

The validity of this model can be checked by linearized plot of t/q_t versus t. The rate constant of pseudo second order adsorption and q_e are determined from the intercept and slope of the plot.

The plots drawn according to the pseudo-second-order model (no mentioned in this paper) are not linear for the two adsorbents. This indicates that it is not appropriate to use the Lagergren kinetic model to predict the adsorption kinetics of ibuprofen onto VBE and RSBE. Thus, the kinetic adsorption data were analyzed by the second order model and the linear plots for VBE and RSBE are shown in Figure 7 and Figure 8, respectively.

Figures 7 and 8 show that the adsorption kinetics was best described by the pseudo second order with high correlation coefficient values. Values of the amount of ibuprofen adsorbed at equilibrium and the rate constant are summarized in table 1.

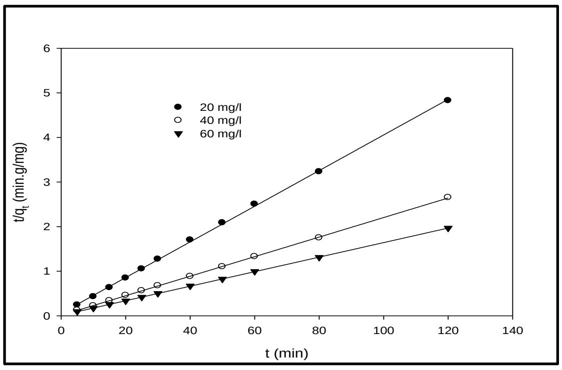

Figure 7: Linearization of ibuprofen adsorption kinetics by VBE for the second order rate

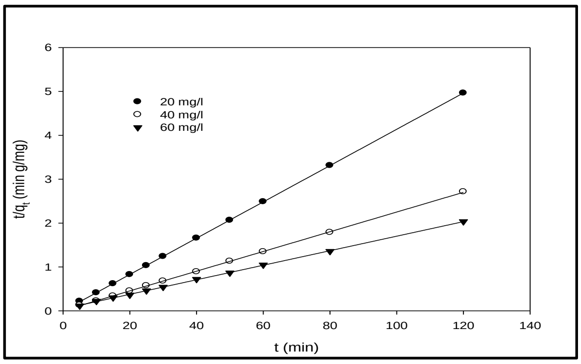

Figure 8: Linearization of ibuprofen adsorption kinetics by RSBE for the second order rate

Table 1: Kinetic parameters for the adsorption of ibuprofen onto RSBE and VBE at various initial concentrations

Adsorbent	C_0 (mg/l)	q_e (mg/g)	$q_{e\,exp}$ (mg/g)	k_2 (g.mg^1.min^{-1})	R^2
VBE	20	24.43	24.44	0.0289	0,9998
	40	45.66	45.67	0.0436	0,9999
	60	60.65	60.66	0.0232	1
RSBE	20	24.15	24.15	29.501	1
	40	44.44	44.29	0.1332	0,999
	60	60.24	57.66	0.0061	0,9998

From the results obtained in table 1, it can be seen that the value of q_e calculated by the pseudo second order model is very close to that determined experimentally. The amount of ibuprofen adsorbed per unit mass of adsorbent (RSBE or VBE) increased with the increase in initial concentration. The obtained results showed also a decrease in rate constants with increasing initial concentration. This behavior can possibly be attributed to the saturation of the active sites from the first minutes, which slows down the adsorption process (Meziti and Boukerroui, 2012).

3.3. Adsorption isotherms

Equilibrium adsorption isotherms defined at 25 °C, is presented in Figure 9. The models used in this study are the Langmuir model and the Freundlich model. The non-linear and linear forms of these models are displayed in Table 2.

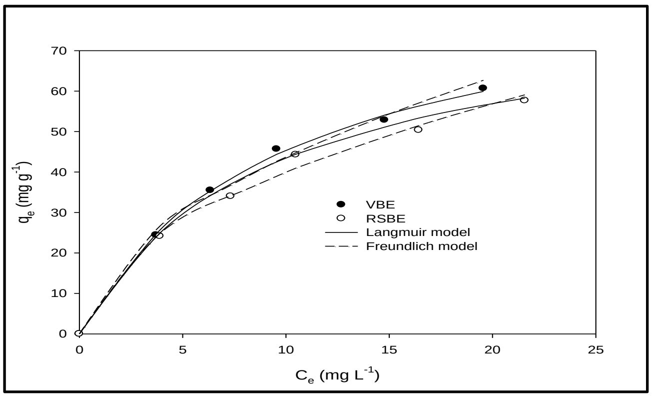

Figure 9: Experimental ibuprofen adsorption isotherms at 25 °C.

Table 2: Langmuir and Freundlich isotherms and their linear forms (Chitour, 1979)

Isotherm	Langmuir	Freundlich
Non-linear form	$q_e = \dfrac{q_{max}\, K_L\, C_e}{1 + K_L\, C_e}$	$q_e = K_F\, C_e^{1/n}$
Linear form	$\dfrac{C_e}{q_e} = \dfrac{1}{q_{max}} C_e + \dfrac{1}{K_L q_{max}}$	$\ln q_e = \dfrac{1}{n} \ln C_e + \ln K_F$
Plot	$\frac{C_e}{q_e}$ versus C_e	$\ln q_e$ versus $\ln C_e$

Where q_e is uptake at equilibrium (mg/g), K_L is Langmuir constant (l/mg), q_{max} is monolayer adsorption capacity (mg/g), C_e is the solution concentration at equilibrium (mg/g), K_F is Freundlich constant, n is Freundlich exponent.

The linear Langmuir and Freundlich isotherms for ibuprofen adsorption onto VBE and RSBE, at 25 °C, were fitted to the experimental data. The Langmuir and Freundlich parameters, along with the correlation coefficients (R^2) of the linear plots, are presented in Table 3.

Table 3. Langmuir and Freundlich isotherm parameters for the ibuprofen adsorption onto VBE and RSBE.

Sample		VBE	RSBE
Langmuir	q_{max} (mg/g)	90.09	82.64
	K_L (l/mg)	0.1016	0.1108
	R^2	0.9977	0.9954
Freundlich	K_F	12.6999	12.4286
	1/n	0.5369	0.5077
	R^2	0.9905	0.9917

The obtained results show that the experimental data fit to the both models Langmuir and Freundlich. These results are clearly shown in Figure 9, where the fitting of the two isotherm models are displayed along with the experimental values. The obtained values of 1/n are less than 1, which implies that the ibuprofen adsorption on the both materials is favorable.

3.4. Effect of initial pH

The pH effect study on the ibuprofen adsorption on the two adsorbents was conducted using ibuprofen solutions of 20 mg / L was studied over a pH range between 2 and 12. The results obtained are shown in Figure 10.

The obtained results show that pH plays a very important role in the adsorption process. It is a parameter affecting both the adsorbent surface charge and the ionization degree of the polluting species being in solution. The experimental results show that the removal rate is greater than 80% between pH 2 and 4. In this pH range the two materials (VBE and RSBE) are positively charged ($pH < pH_{PZC}$) and the ibuprofen is deprotonated from pH > pka (4.91) where it takes a negative charge and so for pH between 2 and 4 ibuprofen is in its molecular form. The ibuprofen is related to the solid surface thanks to the bonds of dispersion type and dipole type. Consequently, as the pH increases to values above 4.91, the ibuprofen adsorption will be at least favorable because the electrostatic repulsion between the ibuprofen anion and the solid surface which gradually becomes more negatively (Mestre et al., 2007).

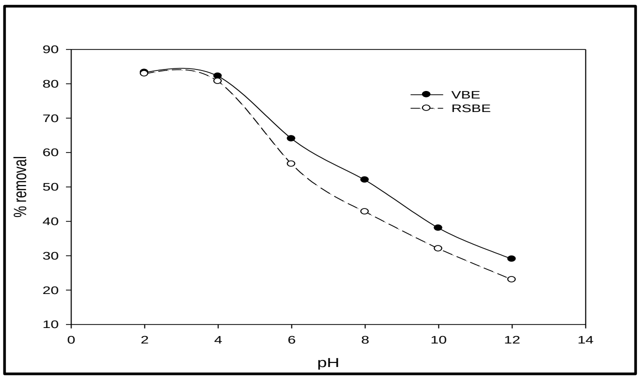

Figure 10: Effect of pH on the ibuprofen adsorption on VBE and RSBE.

(C_0 = 20 mg/l ; m = 0.02 g ; V = 30 ml, w = 300 rpm ; T = 25°C)

4. Conclusion

In this study, the spent bleaching earth (SBE) was regenerated by heat treatment and the adsorption performance of the regenerated material (RSBE) was tested in the removal of ibuprofen from aqueous solution. The obtained results show that the adsorption of ibuprofen onto VBE and RSBE obeys to the pseudo-second order kinetic equation and the sorption isotherms followed the Langmuir and the Freundlich models. The obtained results show also that the resulting material (RSBE) has significant adsorption capacities and it is suitable for ibuprofen removal. These permit to envisage the possibility of its use as adsorbent low cost for the removal of micopollutants from environmental matrices.

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