

Utilization of Calcined Gypsum in Water and Wastewater Treatment: Removal of Ibuprofen

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Adsorption is a widely used technique for the removal of pharmaceutical organic micro-pollutants. In this article, calcined gypsum ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) was utilized for the removal of ibuprofen medicine from polluted water. Several factors including the adsorbent dose, contact time, and temperature were studied. The influence of the ions in the solution on the precipitation of gypsum and its setting time was investigated because it significantly affects the percentage removal. The faster the setting time of gypsum, the lower the percentage removal precipitate. From thermodynamic parameters, the negative values of ΔG° indicated a spontaneous and physisorption of ibuprofen onto the calcined gypsum surface. Kinetic study results showed that the adsorption of ibuprofen on gypsum follows pseudo-first-order kinetics.

Keywords: Calcined Gypsum, Wastewater Treatment, Removal, Ibuprofen

Introduction

Water, in general, suffers from contamination by different types of pollutants. One category of these pollutants is the micro-pollutants such as synthetic hormones, pharmaceuticals, and personal care products (Langenhoff *et al.*, 2013). Therapeutic administration of medications can excrete pharmaceuticals by humans and eventually carry them to Sewage Treatment Plants (STPs) for treatment (Zuccato *et al.*, 2008). This produces toxicological pollutants due to their persistence in the aquatic environment for long periods, in addition to affects the endocrine and developing resistant bacteria strains (Akhtar *et al.*, 2016). Great attention is paid by drinking water companies and water resource institutions to determine the trace concentrations of these compounds in water and wastewater. That is, drugs and their metabolites can be a serious threat to both surface and groundwater in different percentages (Castiglioni *et al.*, 2006, Zuccato *et al.*, 2005, Heberer 2002). Therefore, many analytical techniques have been developed for this purpose (Langenhoff, *et al.*, 2013).

Many studies were conducted to remove pharmaceutical micro-pollutants from water such as paracetamol, diclofenac, and ibuprofen. Various conventional and advanced treatment methods were investigated for this purpose, such as membranous, microfiltration, ozonation, biodegradation and adsorption (Akhtar *et al.*, 2016). Microbial methods were utilized to remove such pollutants as advanced oxidation processes (AOPs) which are based on using reactive oxidants that include ozonation, photocatalytic and ultrasound oxidation (Gogate and Pandit, 2004). This method leads to the degradation of these compounds into carbon dioxide, water, and inorganic ions. Moreover, this method may lead to the formation of potentially harmful by-products (Schwarzenbach *et al.*, 2006). In this regard, biological treatments are not able to remove the micropollutants completely (Guedidi *et al.*, 2017). Researchers resort to another method, which is adsorption using adsorbent materials such as activated carbon. Carbonaceous adsorbents such as activated carbon, charcoal, activated sludge and graphite possess sorption capacities for organic and non-organic chemicals in the liquid and gaseous phases. They are usually the first choice for researchers in the purification of water from harmful organic and inorganic chemicals. Activated carbon is the predominantly studied sorbent for the removal of pharmaceuticals from water, mainly due to its being an affordable high surface area material (Akhtar *et al.*, 2016).

Ibuprofen is an organic pharmaceutical product that causes pollution of water, and the washing water of the manufacturing process is a major source of these pollutants. It is a non-steroidal drug, used as a painkiller, for fever and inflammation (Langenhoff *et al.*, 2013).

Figure 1, illustrates the chemical structure of ibuprofen.

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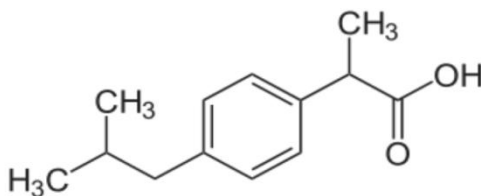


Fig. 1 Chemical Structure of Ibuprofen (Ahmadi *et al.*, 2014).

Ibuprofen is frequently detected in effluents from sewage treatment plants at significant concentrations of up to 25 mg/L (Guedidi *et al.*, 2017). The risk of ibuprofen and other pharmaceutical products results from its metabolism in an organism's digestive system in which the conjugate groups retain the same low level of toxicity as the parent compound. Ibuprofen metabolites include hydroxy- and carboxy-ibuprofen (Nikolaou *et al.*, 2007). Zuccato *et al.* (2008) found that *Synechocystis* showed strong and rapid growth at all concentrations of ibuprofen (2005). There are numerous studies of the removing of this molecule from different types of water (Drinking, waste... etc.). Such methods include biological removal processes, which have proven to be the most effective method (Yamamoto *et al.*, 2008), ultraviolet (UV) radiation, ozone oxidation, and hollow fiber membranes (Williams *et al.*, 2012). Adsorption on diverse types of adsorbent materials was also detected for the removal of ibuprofen and other types of organic pollutants from different environments. In a study carried out by Guedidi *et al.* (2017), a chemically surface-modified activated carbon cloth was used for ibuprofen removal. The study proved that the presence of carbonyl, lactonic and carboxylic groups on the surface of activated carbon will enhance the adsorption capacity of ibuprofen. They also found that the adsorption of ibuprofen onto surface-modified activated carbon is endothermic and follows a physisorption process (Guedidi *et al.*, 2017). Mukoko *et al.*, (2015) have used activated carbon prepared from rice hull and showed high efficiency in removing ibuprofen from wastewater (Mukoko *et al.*, 2015). Clays are also used for the removal of pharmaceutical compounds. Clay is a colloidal fraction of sediments, rocks, and water, which is composed of quartz, metals, silicates, and carbonates. Clays are low-cost, abundantly available, possess high surface area, do not need specific processing before usage, and remove organic and inorganic pollutants by the exchange of ions with acidic or basic pharmaceutical compounds (Akhtar *et al.*, 2016). Powdered activated carbon prepared from cork waste was studied for ibuprofen removal from the liquid phase by Mestre *et al.* (2007). Their results show a high initial adsorption rate, high adsorption capacity, and high removal efficiency, in some cases reaching 100%. Silica-based adsorbent materials were used for the removal of ibuprofen by Bui and Choi (2009). In 2012, Behera *et al.* removed ibuprofen by adsorption onto various soil minerals; such as kaolinite, montmorillonite, goethite, and activated carbon. Results revealed that the sorption of ibuprofen onto all examined soil minerals was highest at pH 3 with also the highest sorption capacity of activated carbon. Recently, Guedidi (2017) used a microporous activated carbon for the removal of ibuprofen from wastewater. Kinetics, isotherms, and pore sites were studied. The aim of this study is to investigate the removal efficiency of ibuprofen from water using calcined gypsum as the adsorbent material. Calcined gypsum is a calcium sulfate hemihydrate (CaSO₄·0.5H₂O), which reacts with water to form a matrix of crystalline-hydrated gypsum (calcium sulfate dihydrate). It is the desired hydration of the calcined gypsum that enables the formation of an interlocking matrix of set gypsum, thereby imparting strength to the gypsum structure in the gypsum-containing product. Moreover, the thermodynamics and kinetics of the adsorption of ibuprofen on calcined gypsum in water and wastewater are presented.

1. Materials and Methods

1.1. Materials

The gypsum was produced from Jabal Mulaih, in Tafila, Southern part of Jordan (Alrawashdeh *et al.*, 2014). It was crushed, milled and then calcined at 150-200°C. Ibuprofen (99%) was obtained from Sigma-Aldrich Co., St. Louis, MO, USA. Ibuprofen stocks were prepared by dissolving 100 mg of ibuprofen in 100 mL of HPLC grade methanol (Sigma-Aldrich, Germany). This stock solution was then used in the preparation of synthetic wastewater samples with an ibuprofen concentration of 204 mg/L.

1.2. Measuring the concentration of Ibuprofen

The ibuprofen concentration was determined spectrophotometrically at 264 nm (SPECTRACOMP 602; Advanced Products, Milan, Italy). A calibration curve of absorbance against different concentrations of ibuprofen was constructed. Samples of ibuprofen solutions were analyzed by UV before and after treatment to determine the amount of ibuprofen removed.

1.3. Experimental

Batch sorption experiments were conducted in a series of 250-mL glass beakers containing 100 mL of 204 mg/L ibuprofen solution. A determined amount of calcined gypsum was added to these beakers. All experiments were conducted at an ambient temperature of 25°C and with a stirring time of 5-25 min. After the completion of the experiments, the samples were filtered. The filtrate of ibuprofen solutions was then subjected to UV-visible analysis to determine the percentage of ibuprofen removal (Zhou and Jiang, 2012).

2. Results and Discussion

2.1. Removal of Ibuprofen

As mentioned before, the objective of this study is to obtain adsorption data to determine the relative effectiveness of the removal of ibuprofen from water using calcined gypsum. The removal percentage of ibuprofen was calculated using the following equation:

$$\text{Removal \%} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of ibuprofen in solution, respectively. A calibration curve was constructed for the UV spectrophotometer at a wavelength of 264 nm to detect ibuprofen after each treatment experiment. The adsorbent amount is an important parameter in batch equilibrium studies. It determines the adsorbent-adsorbate equilibrium of the system as well as the adsorption capacity of the adsorbent. A number of experiments were conducted using different amounts of gypsum (1.0, 2.0, 3.0 and 5.0 g) in order to investigate the effect of the amount of adsorbent on the removal efficiency of ibuprofen. After mixing the gypsum with water containing ibuprofen for a certain period in a batch mode, the samples were then filtered and analyzed using the spectrophotometer to determine the concentration of the remaining ibuprofen. The removal of ibuprofen using different amounts of calcined gypsum from two water samples (distilled and tap) in a batch mode is shown in **Figure 2**. These experiments were performed to investigate the influence of the ions in the solution on the precipitation of gypsum and its setting time, which significantly affect the percentage removal. The fast the setting time gypsum, the lower the percentage removal precipitate.

The results shown in Fig. 2 reveal a direct relationship between the amount of calcined gypsum and the adsorption of ibuprofen. Generally, as the amount of calcined gypsum increases, the removal percentage of ibuprofen also increases. This is due to the increase in the available sites of adsorption upon increasing the amount of dihydrate crystals formed and entrapping the pollutant, which becomes larger as the amount of adsorbent material increases. It is obvious that the efficiency of removal depends on the type of water. The efficiency was greater when distilled water was used because the solubility of the hemihydrate is higher in distilled water and the setting time is slower which gives better chance to the inclusion of the pollutant into the precipitate. This can be attributed to the following: (i) the solubility of calcined gypsum decreases with the ionic strength of the water and the formation of the dihydrate crystals accelerates, which gives less chance for pollutant to become entrapped, and (ii) other species present in tap water might compete with ibuprofen in the adsorption process.

Figure 3 shows the effect of water's type on the solubility of the calcined gypsum using the electrical conductance values of the solution, which reflects the availability of ions before crystallization over time.

2.2. Thermodynamics of adsorption

Thermodynamic parameters such as the change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated from the variation of the thermodynamic equilibrium constant K with temperature. Gibbs free energy can be calculated from the thermodynamic equilibrium constant, K . The adsorption standard free energy changes (ΔG°) can be calculated according to the following:

$$\Delta G^\circ = -RT \ln(K) \quad (2)$$

where R , is the universal gas constant ($8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$) and T is the temperature in Kelvin. Enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equation:

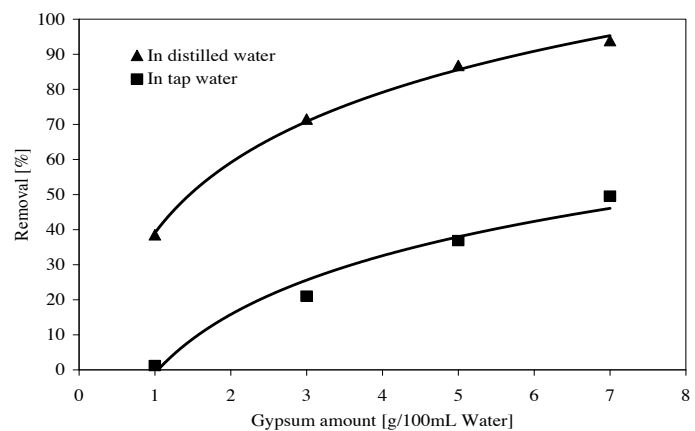


Fig. 2 Removal percentages of Ibuprofen using calcined gypsum as adsorbent material in both tap and distilled water

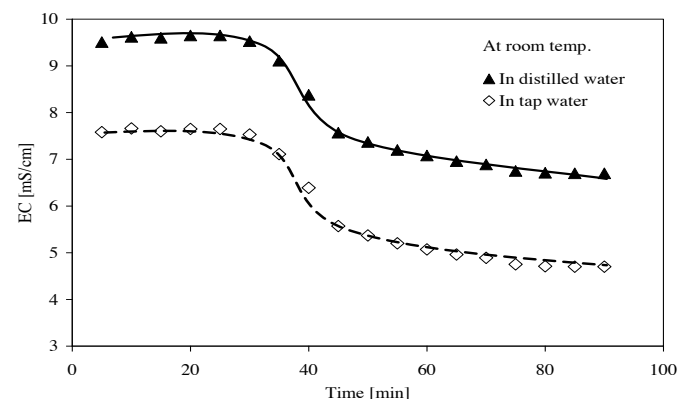


Fig. 3 Electrical conductance (EC) of calcined gypsum product versus time for different types of water.

$$\ln(K) = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (3)$$

Where T, is the temperature in Kelvin, and R is the universal gas constant. **Figure 4**, shows the plot of $\ln(K)$ versus $(1/T)$ according to the Van't Hoff equation. The value of the enthalpy (ΔH°) was calculated from the slope, and the value of entropy (ΔS°) was obtained from equation (3). Table 1 shows the calculated values of thermodynamic parameters for ibuprofen removal using calcined gypsum.

Table 1 Thermodynamic parameters of Ibuprofen removal by calcined gypsum

Temp. [°C]	Removal [%]	K [mol. L ⁻¹]	ΔG° [kJ.mol ⁻¹]	ΔH° [kJ.mol ⁻¹]	ΔS° [kJ. K ⁻¹ .mol ⁻¹]
25	73	2.729	-2.489	3.904	0.0214
35	75	2.857	-2.690		
45	77	2.995	-2.901		
60	79	3.220	-3.239		

The endothermic nature of adsorption was clearly shown by the positive value of ΔH° (3.904 kJ mol⁻¹) which is also governed by the possibility of physical adsorption. The negative values of ΔG° (-2.489 kJ mol⁻¹ to -3.239 kJ mol⁻¹) indicate the spontaneity and the high favorability of the adsorption process for ibuprofen. The positive value of ΔS° (0.0214 kJ K⁻¹mol⁻¹) shows the increased disorder and randomness at the solid-solution interface with the adsorbent.

2.3 The kinetics of adsorption

Kinetic studies were carried out to optimize different operating conditions for the adsorption of ibuprofen. The rate of ibuprofen adsorption on calcined gypsum was studied by measuring change in concentration as a function of time. The volume, mass of adsorbent and initial concentration was kept constant. The uptake rate of ibuprofen by calcined gypsum can be evaluated by studying adsorption kinetics. The best contact time for an adsorption process can also be obtained from such studies. At the beginning of the adsorption process, the rate of removal is high due to the availability of sites on the adsorbent surface. The nature, surface area and amount of adsorbent all affect the kinetics of the adsorption process. The kinetics of ibuprofen adsorption on calcined gypsum was analyzed using two kinetic models: the pseudo-first-order and pseudo-second-order. Firstly, the adsorbed amount of the adsorbate was calculated, the uptake of ibuprofen molecules was calculated from the mass balance, which was stated as the amount of solute adsorbed onto the solid. It equals the amount of solute removed from the solution. The adsorbed amount (Q_e) per unit adsorbent mass (mg g⁻¹) was calculated according to the following:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (4)$$

where C_0 is the initial concentration of adsorbate, C_e is the concentration of the substrate at equilibrium (mg. L⁻¹), m is the adsorbent mass (mg), and V is the solution volume (L). The linear expression of the first-order kinetic is given by the following equation:

$$\ln(Q_e - Q_t) = -k_1t + C_1 \quad (5)$$

where k_1 is the adsorption rate constant for the first order adsorption, Q_t is the amount of adsorbed material at time t (mg/g) and C_1 is

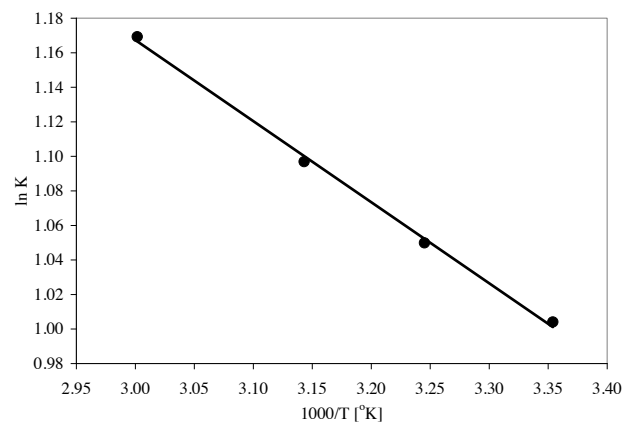


Fig. 4 A plot of $\ln K$ versus $1000/T$ of ibuprofen removal by calcined gypsum.

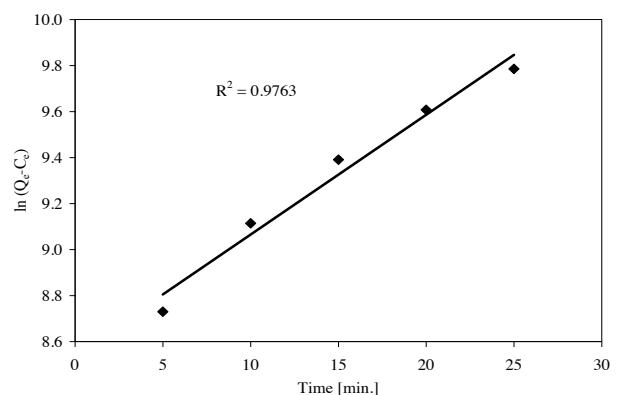


Fig. 5 Pseudo-first-order reaction kinetics for the adsorption of ibuprofen onto calcined gypsum.

the integration constant for the first-order reaction kinetics. **Figure 5** shows the analysis of obtaining data according to pseudo-first-order kinetics.

Adsorption data were also evaluated based on the pseudo-second-order reaction kinetics (**Figure 6**). The linear expression of second-order kinetics is given by the following equation:

$$\frac{1}{Q_e - Q_t} = k_2 t + C_2 \quad (6)$$

where k_2 is the adsorption rate constant for the second-order adsorption and C_2 is the integration constant for the second-order reaction kinetics. Based on Figs. 5 and 6, it can be observed that the first order is more linear than the second-order with correlation coefficient value R^2 of 0.9763. This means that the adsorption of ibuprofen onto gypsum is followed by first-order reaction kinetics. The R^2 values indicate that the adsorption of ibuprofen was not consistent with the pseudo-second-order model as its values were lower than those obtained for pseudo-first-order kinetics. The first-order and second-order rate constants were calculated from the slopes of both Figures 5 and 6, respectively. The values were: $k_1 = 5.21 \times 10^{-2}$ and $k_2 = 5.10 \times 10^{-6}$. Since k_1/k_2 is in the order of 10^4 , it is clear, from the value of the first-rate constant (k_1) that the initial adsorption process is very fast. Activation Energy (E_a) was calculated based on the Arrhenius relationship. **Figure 7** is a plot of $\ln(k_1)$ versus $(1/T)$ in (K^{-1}). The obtained linear equation is: $(y=4140.3x-3458.7)$. Activation energy was calculated based on the slope and intercept of the above linear equation and it was found to be $E_a = -5.482$ kJ/mol, the negative and small value of the activation energy indicates that the reaction is thermodynamically favorable. However, this might also indicate that the process is associated with multi-step mechanisms.

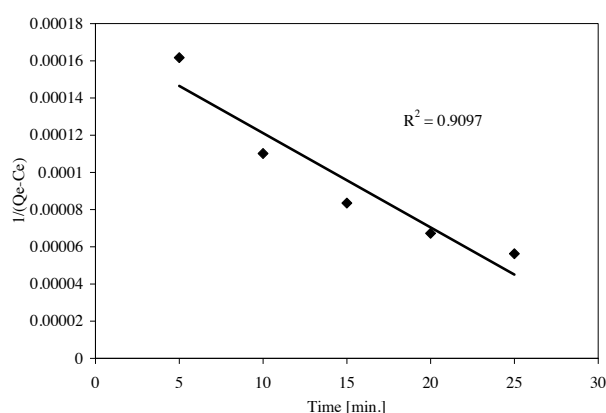


Fig. 6 Pseudo-second-order reaction kinetics for the adsorption of ibuprofen onto calcined gypsum.

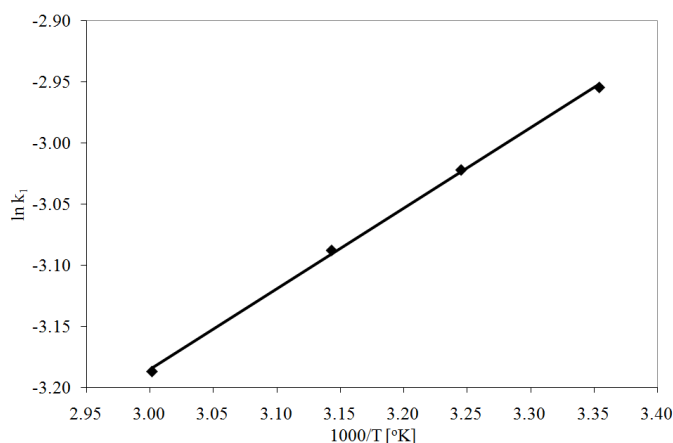


Fig. 7 Arrhenius plot for activation energy determination.

Conclusions

Calcined gypsum from South Jordan can remove ibuprofen from aqueous solutions. The calculated thermodynamic parameters from the adsorption isotherms at four different temperatures allow the conclusion of a spontaneous and exothermic adsorption mechanism for the removal of ibuprofen onto calcined gypsum. As for the adsorption of ibuprofen, the ΔG° values are consistent with a physisorption mechanism ($-7.06 \text{ kJ.mol}^{-1} < \Delta G^\circ < -0.11 \text{ kJ.mol}^{-1}$). The negative ΔS° values indicate an increase in order and this is due to the arrangement of the molecules while they are being adsorbed onto the surface of calcined gypsum. The results reveal that the removal of ibuprofen increases with the increase of the adsorbent amount and contact time. The adsorption of ibuprofen onto calcined gypsum fits the pseudo-first-order kinetic model. The adsorption kinetics of the calcined gypsum under normal conditions highlighted a higher affinity of the adsorbent for ibuprofen. This might be directly correlated and hence attributed to the smallest volume of this molecule and to its hydrophobic nature.

Acknowledgment

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Nomenclature

AOPs	=Advanced Oxidation Processes.	[-]
STPs	=Sewage Treatment Plants.	[-]
C_o	=Initial concentration of dye solution,	[mg.dm ⁻³]
C_e	=Equilibrium concentration of dye solution,	[mg.dm ⁻³]

K	=Equilibrium constant	[-]
R	=Universal gas constant,	[J.g-mol ⁻¹ .K ⁻¹]
Q_c	=The adsorbed amount per unit adsorbent mass	[mg g ⁻¹]
Q_t	=The adsorbed amount per unit adsorbent mass at time t	[mg g ⁻¹]
ΔH°	=Standard enthalpy,	[kJ.g-mol ⁻¹]
ΔG°	=Standard Gibbs free energy,	[kJ.gmol ⁻¹]
ΔS°	=Standard entropy,	[J.gmol ⁻¹ .K ⁻¹]
UV	=Ultraviolet	[nm]
E_a	=Activation energy,	[kJ.mol ⁻¹]

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