Study of the Ability of Flint Clay Surface in Adsorption of Ibuprofen from Solution

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الخلاصة

تمت در اسة قابلية طين الفلنت على أمتزاز دواء الايبوبروفين كأحد تطبيقات الامتزاز في السوائل ،وبأستخدام مدى من درجات الحرارة (C°C, 34, 37.5°) وبدالة حامضية مقدارها (7 و 1.2) ،تمت متابعة الامتزاز من خلال قياس الامتصاصية للدواء النقي قبل وبعد الامتزاز وباستعمال مطيافية الأشعة الفوق البنفسجية . كانت قابلية امتزاز الايبوبروفين تزداد بزيادة حامضية المحلول (عند الدالة الحمضية 1.2) ويعود السبب في ذلك الى أحتمالية التغير الحاصل في سطح الطين من خلال تأثير الحامض على المجاميع القطبية الموجودة على السطح و هذا يعطي تصور على ان التاثر بين السطح وجزيئات الدواء هو نوعي وأقوى من التاثر بين جزيئات المذيب – والمذاب وهذا يقود الى زيادة مقدار الامتزاز . ،كذلك وضحت باعثة للحرارة .

Abstract

This research is concerned with one of applications of adsorption from solution on selected clay surface. The aim of the work is to investigate the activity of flint clay as antidote in treatment of poisoning by some drug (ibuprofen). The technique of U.V / visible spectrophotometer has been utilized for quantitative estimation of adsorption uptake of the drug by the surfaces in different conditions of temperature, and pH. Stomach environments; have been specifically taken into consideration in this study, i.e., its pH and human body temperature. The adsorption of ibuprofen from aqueous solution on clay has been studied initially in neutral media using distilled water (pH \approx 7) as a solvent at 37.5°C. The increase in adsorption uptake of drug in acidic media may be attributed to the possible changes in the properties of clay surfaces upon lowering the pH value at the solid liquid interface. The results show a decrease in the adsorption extent of drug on clay with increasing the temperature; suggesting an exothermic adsorption process to take place on the two surfaces.

Keywords: Flint clay, Adsorption, Ibuprofen

Introduction

Pharmaceuticals pose a huge risk as they are continually introduced in the environment at trace level due to their high worldwide consumption. Since a considerable amount of the dose taken is not absorbed by the body, a variety of these chemicals—including painkillers, tranquilizers, anti-depressants, antibiotics, birth control pills, chemotherapy agents, etc.,—are finding their way into the environment via human and animal excreta, from disposal into the sewage system,

and from landfill leachate that may impact groundwater supplies. However, little is known about the occurrence, fate, synergistic, and long-term effects of these pollutants and their metabolites following their end-use (1-3). Control of this kind of pollution is very difficult due to the diversity of sources. Conventional wastewater treatments are not always effective to eliminate and/or degrade the majority of pharmaceutical compounds, which have been found to accumulate in drinking water (1-4). The enormous diversity of chemical composition of these pollutants in waters requires special treatment technologies for water decontamination, in order to improve the quality of water and treated wastewater before promoting its reutilization.

Adsorption is a well-established and highly efficient technology for wastewater remediation. Among the different adsorbents, activated carbon is commonly used for the purification of water with low pollutant concentrations. Its well-developed porous structure is responsible for physical adsorption, whereas the variety of its surface chemistry allows specific interactions to take place for a given adsorbate /adsorbent system (5). Driven by the possibility to synthesize carbon materials with controlled structure and chemical features, their use for the removal of pharmaceuticals offers an interesting and simple tool to deal with this new environmental challenge (6-13). The aim of this study is to investigate the reactive adsorption of Ibuprofen on locally available clay (in the adsorption of the drug (Ibuprofen 2-(4-isobutylphenyl) propanoic acid) from solution. The results are analyzed in terms of the composition of the adsorbent and the solution conditions. The expected adsorptive activity of the clay toward the drug may give an indication for using them as physical antidotes in the treatment of poisoning by the above drug. The stability of Ibuprofen during the adsorption process was explored, and knowledge of the reactive adsorption mechanism that occurs on the clay surface, particularly the role of the clay features (porosity and composition) was gained. The term "clay" defined as "a naturally occurring sediment composed of one or more minerals and accessory compounds" (14). The clay usually composed of hydrated silicates of aluminum, iron or magnesium. Hydrated alumina, or iron oxide predominating in particles of colloidal or near-colloidal size of clays are commonly developing plasticity when sufficiently pulverized and wetted (15). The basic structures of the clay minerals are formed from two basic units of silicate, held together by ionic bonds, tetrahydral and octahedral layers.

Human toxicology

Ibuprofen overdose has become common since it was licensed for over-the-counter use. There are many overdose experiences reported in the medical literature, although the frequency of life-threatening complications from ibuprofen overdose is low. Human response in cases of overdose ranges from absence of symptoms to fatal outcome in spite of intensive care treatment. Most symptoms are an excess of the pharmacological action of ibuprofen and include abdominal pain, nausea, vomiting, drowsiness, dizziness, headache, tinnitus, and nystagmus. Rarely more severe symptoms such as gastrointestinal bleeding, seizures, metabolic acidosis, hyperkalaemia, hypotension, bradycardia, tachycardia, atrial fibrillation, coma, hepatic dysfunction, acute renal failure, cyanosis, respiratory depression, and cardiac arrest have been reported. The severity of symptoms varies with the ingested dose and the time elapsed; however, individual sensitivity also plays an important role. Generally, the symptoms observed with an overdose of ibuprofen are similar to the symptoms caused by overdoses.

Method and Materials

Instruments: The following instruments were used throughout the work.

Water bath, shaker, Shimadzu UV-Visible spectrophotometer type UV-260, PHmeter and digital balance.

Chemicals: HCl, 36 % w/w, specific gravity (1.18), Fluka . Ibuprofen 2-(4-isobutylphenyl) propanoic acid.

Adsorption experiments were carried out in neutral solution (distilled water) and in acidic media ($pH \approx 1.2$) by using 0.1M- HCl .The pH of the suspension at the commencement of the adsorption was measured as well as after the experiment by using pH meter.

Preparation of Clay Powder

The flint clay was treated with 10% NaOH for 10 hrs. (to activate the surface) then neutralized by 1.0 % HF solution and washed with excessive amounts of distilled water to remove the soluble materials, washed then separated by filtration, dried in an oven for 5 hours at 120 C^o and stored kept in airtight containers. The clay was grinded and sieved by the available sieves to a particle size of 63-micrometer by using a (230-mesh) sieve.

Determination of maximum absorption, λ max

UV/visible scanning spectrum of the drug has been recorded wavelength value corresponding to the maximum absorbencies (λ_{max}) for drug was found (222 nm), the value was utilized for measurements of quantitative estimations throughout this research.



Fig 1: UV visible spectrum of ibuprofen , a-before adsorption b-after adsorption

Effect of pH on Adsorption

Adsorption experiments were carried out in neutral solution (distilled water) and in acidic media ($pH \approx 1.2$) by using 0.1M- HCl. The pH of the suspension at the commencement of the adsorption was measured as well as after the experiment by using pH meter.

Adsorption Isotherm

Volumes of 10 ml of each drug solutions of known concentrations (100,200,300,400,500 mg/l) in 0.1M HCl $pH\approx1.2$, were added separately to stoppered test tube containing (0.1g) each of the clay adsorbent. The test tubes were shaken in a thermostatically controlled shaker at a speed of 100 rpm for the required equilibration time. After the equilibrium time elapsed, the mixtures were allowed to settle and the clear liquids were centrifuged at (2000 rpm) for (10 minutes). Equilibrium concentrations were obtained by the usual manner of comparing the experimental data with the calibration curves. The amount of drug adsorbed was calculated from the initial and final concentrations and the volume of solution:-

$$\frac{x}{m} = \frac{V(C_o - C_e)}{m}$$

Where x = the quantity adsorbed (mg).

V= volume of solution (l). C_o = initial concentration (mg/l) C_e = equilibrium concentration (mg/l) m= weight of adsorbent (g)

Adsorption uptake is expressed by the ratio x/m or Qe which is defined by the quantity of adsorbate in (mg) held by (0. 1g) of adsorbent.

Effect of Temperature on Adsorption

Similar adsorption experiments were performed as mentioned above at temperatures of 30, 34 and $37.5^{\circ}C$.

Results and Discussion

Adsorption of Ibuprofen

The adsorption of ibuprofen from aqueous solution on clay has been studied initially in neutral media using distilled water (pH \approx 7) as a solvent at 37.5°C.The results are given in Table (1) by the initial concentration of ibuprofen solution (C_o), the equilibrium concentration (C_e) and the adsorption uptake of the drug by the clay (Q_e). C_o and C_e are expressed in mg/l and Q_e is expressed in mg/g.

C	ibuprofen		
C_0	C _e	Qe	
iiig/1	mg/l	mg/g	
100	92.5	0.75	
200	177.2	2.28	
300	214	8.6	
400	305.4	9.46	
500	398	10.2	

Table 1: Adsorption uptake of ibuprofen by the clay at $pH \approx 7 \& 37.5^{\circ}C$.

These results exhibit the ability of the clay to adsorb the drug from solution in different levels, figure (2) illustrate the general shape of ibuprofen adsorption isotherms at $pH \approx 7$.



Fig. 2: Adsorption isotherms of drug on flint clay at $pH \approx 7$ and at $37.5^{\circ}C$.

In order to simulate the pH of stomach, the adsorption processes were also carried out at pH \approx 1.2 by using a solution of 0.1M hydrochloric acid at normal human body temperature (37.5°C). Table (2) shows the related results at pH \approx 1.2 and 37.5°C.

C	ibuprofen		
C_0 mg/l	C _e	Q_e	
iiig/1	mg/l	mg/g	
100	88.2	1.18	
200	142	5.8	
300	176.5	12.35	
400	223	17.7	
500	211.3	28.87	

Table 2: Adsorption uptake of ibuprofen from aqueous 0.1M HCl Solution on clay at pH≈1.2 and 37.5°C.

The adsorption extents of drug on the clay have higher values at $pH \approx 1.2$ compared with that found at neutral media. The increase in adsorption uptake of drug in acidic media may be attributed to the possible changes in the properties of clay surfaces upon lowering the pH value at the solid liquid interface. Thus, the interaction between the surface and drug molecules at $pH \approx 1.2$ is due to the proton effect of the acid on the polar groups of the surface which in turn affects the adsorption process through out drug-surface interaction. The attraction between the surface may be specific and stronger than the attraction between the solvent-solute leading to an increase in the quantity adsorbed (12).



Fig. 3: Adsorption isotherms of drug on flint clay at $pH \approx 1.2$ and 37.5°C.



Fig .4: Ibuprofens structure

The effect of temperature variation on the adsorption extent of the drug on the clay has been studied at pH 1.2. Table (3) and figure (5) illustrate the data and the general shapes of drug adsorption isotherms at 30, 34, and 37.5° C. The results show a decrease in the adsorption extent of drug on clay with increasing the temperature; suggesting an exothermic adsorption process to take place on the two surfaces (13). This corresponds to a weakening of the attractive forces between the solute and the solid surface (and between adjacent adsorbed solute molecules) with increasing temperature, and corresponding increase in solubility of the solute in the solvent. This result may be attributed to a specific physical interaction between the flint clay and the drug molecule, which requires an appreciable energy in order to take place. Exothermic drug uptake may also be interpreted as a consequence of possible absorption process or a sorption process by the surface. Moreover, in the acid solution, an ion exchange mechanism may also occur at the clay-liquid interface (14).

С	30°C		34°C		37.5°C	
C_0	C _e	Qe	C _e	Qe	C _e	Qe
mg/1	mg/l	mg/g	mg/l	mg/g	mg/l	mg/g
100	80.09	1.99	83.3	1.67	88.2	1.18
200	134.2	6.58	138.9	6.11	142	5.8
300	168	13.2	172.3	12.77	176.5	12.35
400	217.4	18.26	221	17.9	223	17.7
500	189	31.1	201.6	29.84	211.3	28.87

Table 3: Adsorption of drug on clay at three different temperatures in $pH \approx 1.2$ solutions



- Fig.5: Adsorption isotherms of drug on the clay at $pH\!\approx\!1.2$ and at (30 , 34 and 37.5°C)
- Table 4: Effect of temperature of the maximum adsorbed quantity for adsorption of drug on clay at C_0 = 500mg/l

Т.	T.	1000/T	ibuprofen	
°C	°K	°K ⁻¹	X _m	$\ln X_{m}$
30	303	3.300	189	5.241
34	307	3.257	201	5.303
37.5	310.5	3.22	211.3	5.353



Fig.6: In X_m plotted against reciprocal absolute temperature for the adsorption of the drug on clay

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