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Research Article

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Thermodynamic studies of Tetracycline Antibiotic Adsorption on Bentonite

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Abstract Due to increased pharmaceutical sewage, the cost efficient adsorbent is extremely needed for medical wastewater treatment. Bentonite which is consists essentially of clay minerals of the smectite group; have a wide range of industrial uses. In this study, a simple approach to adsorb Tetracycline (TC) from aqueous solution by exchangeable cation by bentonite clay is presented. The effects of contact time, initial TC concentration, adsorbent dosage, and solution temperature on the adsorption of TC ions from solution were investigated. The theoretical capacity of bentonite clay adsorbent is about 31.4 mg/g. The optimum adsorption conditions were recommended.

Keyword: Tetracycline; Adsorption; bentonite; Thermodynamic

Introduction

Domestic wastewaters contain a variety of organic wastewater contaminants such as pharmaceuticals and personal care products [1, 2]. It has been proven that most of these compounds undergo both incomplete removal in wastewater treatment plants and slow natural degradation, consequently they are found in surface waters receiving effluent from treatment plants [3, 4]. Pharmaceuticals can also be found in surface waters due to their veterinary use, in such cases they enter the environment via manure dispersion and animal excretion onto soils [5, 6]. Antibiotics are of particular concern because their presence in natural waters contributes to the spread of antibiotic resistance in microorganisms [7, 8].

These antibiotics can be divided into seven major categories: aminoglycosides, amphenicols, β-lactams, macrolides, antibiotic peptides, polyethers or ionophores, tetracyclines (TCs) [9]. TCs are one of the most widely used antibiotics in the world, which are poorly absorbed into the digestive tract, and are unchanged when excreted in feces and urine [10-12]. On account of a broad spectrum of antimicrobial activity, low cost, and wide applications of TC, this has led to concerns with regard to the unsafe residue which is toxic and can provoke allergies [13, 14].

It follows that antibiotics need to be removed before the effluent are discharged into rivers [15]. However, this has always been a major problem because of the difficulty of treating such wastewaters by conventional methods [16]. Biological procedures, although widely utilized in the removal of antibiotics, are very inefficient, because of the low biodegradability of antibiotics [17, 18]. A variety of other methods, including coagulation, chemical oxidation, photocatalysis, and electrochemical and adsorption techniques, has been examined. Adsorption techniques have been widely applied to the treatment of industrial wastewater containing dyes, antibiotics, heavy metals, and other inorganic and organic impurities [19, 20].

Adsorption has been found to be one of the most efficient physicochemical processes, superior to many other techniques for water reuse in terms of the simplicity of operation [21]. If the adsorption system is designed correctly, it will produce a treated effluent of high quality [22]. Activated carbon has been widely used for this purpose because of its high adsorption capacity. However, its high cost sometimes tends to limit its use [23, 24]. Several nonconventional, low-cost adsorbents have also been tried for antibiotics removal [25].

Clay minerals are known with a wide variety of cations and organic molecules by adsorption, interaction and cation exchange capacity. These minerals may serve as a cost-effective sorbents for the removal inorganic and organic impurities [26]. Their sorption capacities are usually less than those of synthetic sorbents; these materials could provide an inexpensive substitute for the treatment of inorganic and organic impurities for wastewaters [27, 28].

Bentonites, which contain essentially of clay minerals of the smectite group, have a wide range of industrial uses. A particular feature of this group of minerals is the substitution of Si^{+4} and Al^{+3} in the crystal structure by lower valiancy cation. The structure, chemical composition, exchangeable ion type and small crystal size of smectite are responsible for several unique prosperities, including a large chemically active surface area, a high cation exchange capacity, and interlayer surface having unusual hydration characteristics [29].

This work aimed to explore the ability of using bentonite clay for TC removal from the Wastewater as a low cost adsorbent. Batch experiments were carried out to choice the preferred adsorption conditions.

Materials and Methods

Chemicals and Reagents

Tetracycline hydrochloride (Molecular weight: 480.9, Molecular formula: $C_{22}H_{24}N_2O_8 \cdot HCl$) was used as the adsorbate in this study and obtained from Sigma-Aldrich, USA and was used without further purification. The chemical structure of TC, shown in Fig. 1. The pH of the TC solution was adjusted to a required value using 0.1 M HCl and 0.1 M NaOH.

Adsorption studies

Batch adsorption experiments were carried out typically by stirring 0.3 g of bentonite with 100 mL of TC solution (pH= 7). Experiments were also carried out to determine the effects of varying both the adsorbent concentration and the contact time of the solution. Working solutions of TC were prepared from the stock solution (100 mg/L) to the desired concentrations (10–200 mg/L) for each experimental run. All the experiments were carried out at a constant speed of 150 rpm with mechanical stirring. The adsorption study was conducted at four different temperatures (283, 298, 313 and 328 K) in a thermostated system, with an outer circulating-water bath. During each run, aliquots of 0.1 mL were withdrawn from the solutions at regular intervals of time, diluted, and centrifuged for 10 min at 2000 rpm, and the absorbance of the supernatant solution was measured. The TC concentration was estimated spectrophotometrically by using a UV–Vis spectrophotometer at λ_{max} = 360 nm, corresponding to the maximum absorbance.

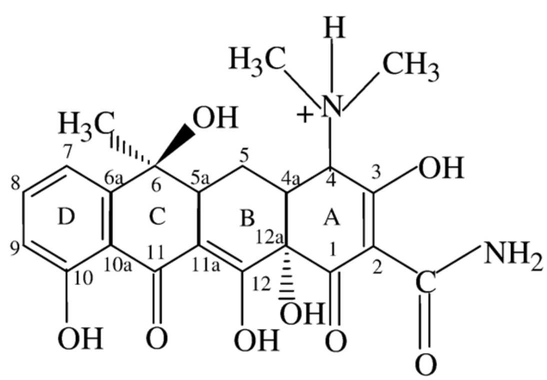

Figure 1: The chemical structure of tetracycline hydrochloride

Results and Discussion

Effect of Adsorbent Concentration

The effect of bentonite concentration on TC adsorption at a contact time of 60 min was studied by varying the adsorbent dose from 0.5 to 4 g/L in a 100 mg/L TC solution. The results are shown in Fig. 2. Increasing the adsorbent concentration is thus seen to enhance the percentage removal of TC. Increased adsorbent concentration implies a greater surface area of bentonite and, consequently, a greater number of possible binding sites (29, 30). At adsorbent doses greater than 3 g/L, there was little change in either the rate of attaining adsorption equilibrium of the TC, or the percentage removal of TC. Similar results have been reported for the adsorption of TC on alumina-coated carbon nanotubes (31).

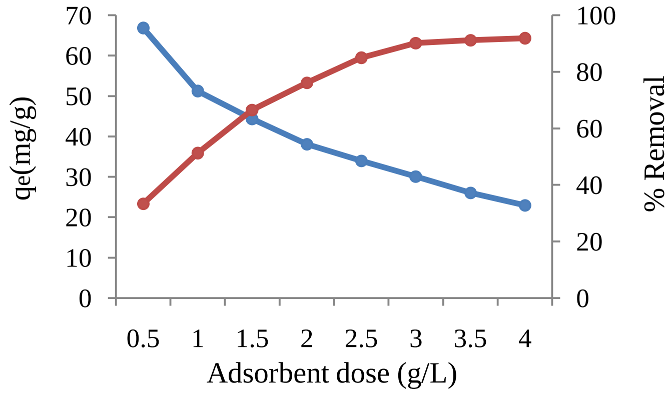

Figure 2: Effect of adsorbent dose on the removal of TC (T = 303 K, time: 60 min, pH= 7 and C_0 = 100mg/L)

Effect of Initial TC Concentration and Contact Time

The effect of initial TC concentration on the adsorption onto bentonite and the percentage removal is shown in Fig. 3. Hence, it appears that more TC was retained by the adsorbent, and the adsorption mechanism also became more efficient, as the initial TC concentration increased, but the percentage removal was higher at low concentration. Fig. 3 indicate that the initial TC concentration has an important influence on the adsorption capacity of the bentonite. For example, at higher solution concentrations, viz. 100 and 200 mg/L, the TC uptake shows a slight decrease. This change in equilibrium behavior may point to a chemisorptions process that is taking place at the surface of the bentonite in the first region, to be followed by a second layer of adsorbate in the second region (31). The ionic nature of TC could well be responsible for the behavior described, leading to one or more reactions over and above the primary adsorption phenomena.

The effects of contact time on the adsorption of TC onto bentonite and the percentage of TC removed at 30 ◦C are illustrated in Fig. 3. Hence it appears that a rapid initial uptake occurs, with equilibrium reached in less than 60 min. The fast uptake of the TC molecules is due to solute transfer, as there are only sorbate and sorbent interactions with negligible interference from solute-solute interactions (32).

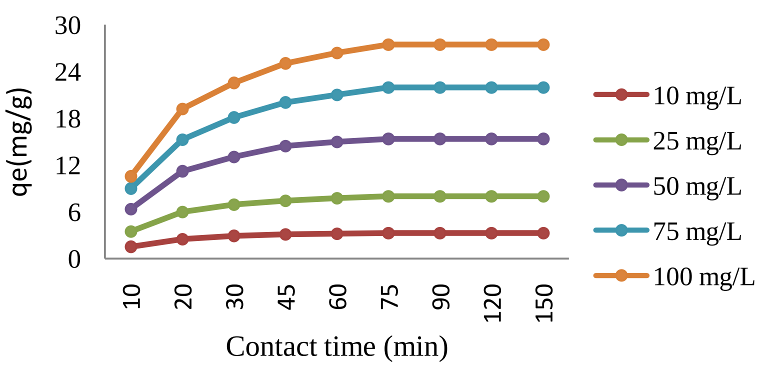

Figure 3: Effect of contact time and initial TC concentration (temperature: 303 K, adsorbent dose: 3 g/L)

Thermodynamic Studies

Thermodynamic parameters were calculated from the difference of the thermodynamic distribution coefficient, K_c with change in temperature. The standard free energy change, ΔG°, was calculated using the expression (33)**:**

$\Delta G° = -RT \ln K_c$

$\Delta G° = \Delta H° - T\,\Delta S°$

Where, R is gas constant (8.314 J/mol/K), T is the absolute temperature in K° and K_c is the Langmuir constant. Standard enthalpy (ΔH°) and entropy (ΔS°) of adsorption could be estimated from Van't Hoff equation. The thermodynamic parameters are offered in Table 2. It is evident from the table that the values of ΔG° are negative. The negative values of ΔG° for all adsorbents at various temperatures indicate the process to be feasible and spontaneous. Actually that the values of the ΔG° decrease with increasing temperature shows the increase of spontaneous influence. For all the sorbents, the positive value of ΔH° suggested the endothermic nature of the adsorption process. Moreover, the positive value of ΔS° also indicates the increased randomness during sorption process (34).

Table 1: Thermodynamic parameters for adsorption of TC by Bentonite at different temperatures

ΔH° (KJ/mol)	**ΔS° (KJ/mol)**	**ΔG° (KJ/mol)**			
		283 K	**298 K**	**313 K**	**328 K**
9.854	0.242	-5.75	-6.11	-6.84	-7.46

Conclusion

The removal of TC by bentonite was investigated and the results show significant adsorption capacities of the clay sample under optimized conditions. This may be attributed to the high specific surface area of the adsorbent. The absolute TC uptake by bentonite reached a value of about 31.4 mg/g. The TC uptake by the studied bentonite is quite complicated phenomenon associated with the aqueous chemistry of the elements and the nature of the materials. The ability of the material to adsorbed TC is mainly due to the micro-porous minerals (clay minerals) constituting approximately 93% of the samples.

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