Isotherm and pH Effect Studies of Tetracycline Drug Removal from Aqueous Solution Using Cobalt Oxide Surface

Hawraa Kassem Hami*, Ruba Fahmi Abbas**, Ali Amer Waheb***, Dhifaf A. Abdul abass, Marwa A. Abed and Asmaa A. Maryoosh
Department of Chemistry, Collage of Science, Al-Mustansiryiah University, Baghdad-Iraq.
* Corresponding Author: hawraak2012@uomustansiriyah.edu.iq.
** Corresponding Author: rubaf1983@uomustansiriyah.edu.iq.
*** Corresponding Author: alichance80@uomustansiriyah.edu.iq.

Abstract
Tetracycline adsorption on the surface of cobalt oxide studied in this work to determine the appropriate conditions for increasing the efficiency of adsorption by changing the temperature, adsorbed dosages, concentration, contact time and pH. The results showed that the rate of adsorption decreased by increasing the temperature and concentration and at 45 minutes with 0.1 gm of Co_3O_4. The influence of pH on adsorption at pH (1.2, 6, 8) was studied and concentration with a linear range of (20-70 mg/l), the adsorption ratio decreased by increasing the concentration at the same pH. The point of zero charges pHzc calculated and found to be equal to 7.2. Both Langmuir and Freundlich isotherm studied. The result showed a good agreement with Freundlich linear model. [DOI: 10.22401/ANJS.22.2.02]

Keywords: Isotherm, Doxycycline, Adsorption, Cobalt Oxide, The point of zero charges pHzc.

Introduction
Antibiotics are classified as contaminants of the environment where they were found in soils, surface water and groundwater even in drinking water [1]. They are transferred to the environment through human and animal waste [2]. That the widespread use antibiotics it can cause a diversity of harmful influences like chronic toxicity, reduce human immunity, and diffuse in antibiotic-resistant genes [3]. Antibiotic contamination is a potential menace to human soundness. It is, therefore, necessary to look for ways to remove these pollutants. Antibiotic medication tetracycline (TC), is one sort of the most generally utilized anti-infection agents, display a range of active antibiotics in the environment. Tetracycline has been reported to cause bacterial resistance leading to the destruction of the environment and the threat of human soundness through bioaccumulation in the food chain. Therefore, tetracycline is removed from the water environment is necessary [4]. A number of operating conditions have been sophisticated to eliminate tetracycline from an aqueous solution in the last years, those encompass ion exchange, photo electro catalytic degradation, coagulation, membrane processing, ozonation and adsorption. Adsorption processes are one of the most widely used processes for the removal of antibiotics. It is characterized by its high efficiency, ease of use, low cost and no risk of toxic by-products [5]. Tetracycline was chosen because of its wide application in clinical medicine, aquaculture and stockbreeding, as well as its environmental importance. The effect of pH on tetracycline adsorption was studied in detail. The adsorption isotherm was studied to understand the behavior of tetracyclineon cobalt oxide surface [6].

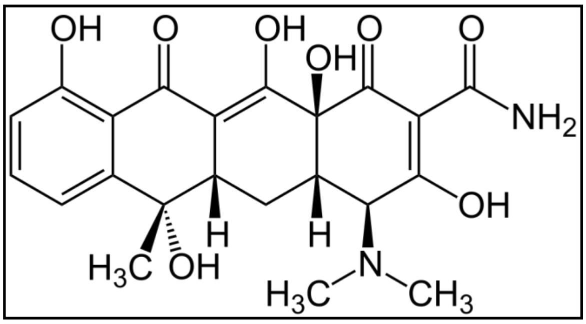

Fig.(1): Structure of tetracycline.

Experimental

Apparatus

pH meter (Hana), UV-Visible Spectrophotometer (CARY 100, VARIAN Co.) with 1 cm quartz cell and shaking water path (BS-11degetal, JEIO Korea, TECH).

Reagent

The chemicals reagents in this research are:

1. Tetracycline powder ($C_{20}H_{24}N_2O_8$, 444.4 g/mol) received from SDI-Iraq Company without further purification. A stock solution of tetracycline (1000 mg/L) was prepared by dissolved 0.1 gm of tetracycline in 100 mL distilled water. Every working standard solution was freshly prepared by diluting the stock solution with distilled water.
2. Cobalt Oxide (BDH) as absorbent.
3. Sodium hydroxide (ka–Granite Switzerland) (0.1N) and Hydrochloric acid (BDH, England) (0.1N) to control pH.

Adsorption Experiments

The Batch experiments were performed using the batch equilibration techniques in a temperature-controlled water bath shaker. For the adsorption equilibrium experiments, a fixed adsorbent dose (0.1 gm) was weighed into 100 mL conical flasks containing 10mL of different initial concentrations of tetracycline. The mixture was shaken for 0.45 min at 37.5°C until the equilibrium was obtained. pH values of tetracycline solutions were adjusted by 0.1 N HCl and NaOH .

Analytical Methods

An amount of known concentration of tetracycline was transferred in a flask and mixed with 0.1 gm of Cobalt Oxide and using a thermostatic shaker bath for 45 min. at the maximum wavelength (λmax = 414 nm). At equilibrium, the amount of adsorbed q_e (mg/g), calculated from:

$$qe = \frac{(Co-Ce)V}{m} \quad \text{.......................................} \ (1)$$

Where, C_0 (mg/L) is the initial concentration of tetracycline (mg/L), C_e equilibrium concentration, V (L) is the solution volume and m is the weight of Co_3O_4 powder.

Removal percentage (g) for tetracycline can be calculated as follows [7, 8]:

$$Removal\% = \frac{(Co-Ct)}{Co} \times 100 \quad \text{................} \ (2)$$

Result and Discussion

Calibration curve

A stock solution of tetracycline solution (1000 mg/L) was prepared to fix a certain weight of the tetracycline in water. A series of solutions were prepared within the range (20-70 mg / L) and their absorption was measured at (λ_{max} = 414 nm). The absorption coefficient was calculated by drawing the absorption values against the concentration and was a = 0.0273gm^{-1}. L. cm^{-1}.as showing in Fig.(2) [9].

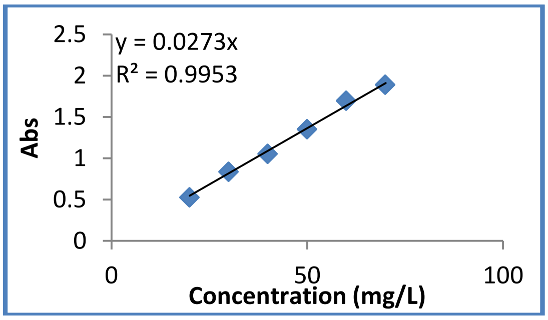

Fig.(2): Calibration curve of the tetracycline.

1- The influence of the initial concentration

Adsorption reaction of tetracycline drug was performed using different concentrations of (20-70 mg/L) at pH 6 and reaction temperature of 37.5° C for 45 minutes. The ratio of tetracycline removal decreased with the increase in the initial concentration of tetracycline Fig.(3) It can be explained that all the active-sites on the surface of the substance adsorbed become saturated with a certain concentration and an increase in concentration does not affect the rate of adsorption[10, 11].

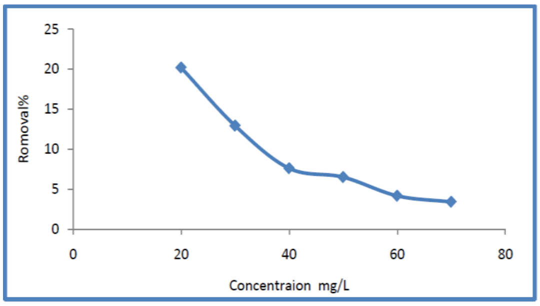

Fig.(3): Effect of initial concentration on tetracycline adsorption.

2- The influence of adsorbent dosages

The influence of surface mass was studied on tetracycline adsorption where the experiment was performed by adding (0.05, 0.1, 0.2, 0.3 and 0.4 gm) to 50 mg/L at pH 6 and 37.5° C for 45 minutes. The rate of removal rose rapidly with increased of the weight of Co_3O_4 doses. The best rat of adsorption removed was recorded with 0.1 gm of Co_3O_4, and any increase in surface amount more than 0.1gm did not affect in the adsorption rate. This is due to lower concentration of tetracycline and the height available effective sites on the adsorbed surface. As showing in Fig.(4)[12,13]

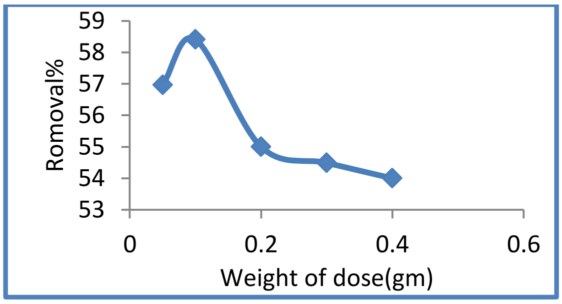

Fig.(4): Effect of the adsorbed amount on tetracycline adsorption.

3- The influence of temperature

Adsorption was studied at various temperatures (37, 47 and 57° C), concentration 50 mg/L, pH 6 for 45 minutes observed from Fig.(5) decreased percentage tetracycline adsorption with temperature increase from 37°C to 57°C. These results indicate that this process is exothermic and the adsorption is physical, so the high temperature will have a negative impact on adsorption [14.15].

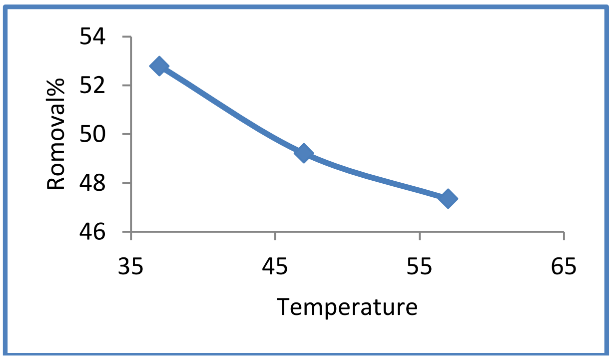

Fig.(5): Effect of temperature on tetracycline adsorption.

4-Influence of contact time

The removable of tetracycline onto cobalt oxide was performed at a different times (15-90 min) and increased gradually every 15 minutes. Initially, the removal rate increased with time increasing to 45 minutes from the contact time, and after that the adsorption rate became practically constant. This happened because as time progresses effective sites on the adsorbed surface are covered with tetracycline and further no adsorption occur [16,17]. Fig.(6) summarize the percentage removal behavior at various contact time.

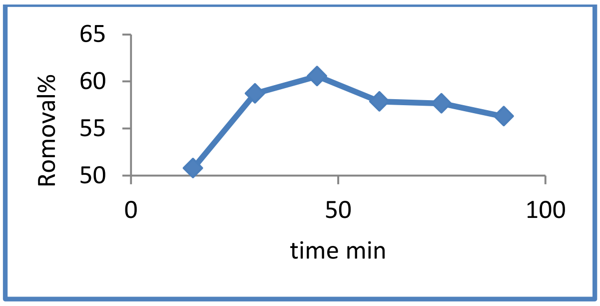

Fig.(6): Effect of time on tetracycline adsorption.

5-Influences of solution pH

The removal of the medicines in their aqueous solution depends heavily on the pH of the solution that effect in the adsorbent surface charge, the ionization degree. Influence of initial pH on the adsorption capacity of tetracycline on cobalt oxide was studied at pH (1.2, 6, and 8) at the adsorbent dosage of 0.1 gm, using concentration (20-70 mg/l) at 37C°.

Tetracycline has changing charges on different sites depending on pH solution, when pH is less than 4, Tetracycline be cation (TCH^{1+}), because of to the protonation of dimethyl ammonium group. At pH (3.5 -7.5), Tetracycline be a zwitterion ($TCH_2^{\ 0}$), because of to the loss of a proton from the phenolic diketone moiety. At pH higher than 7, Tetracycline be anion (TCH^- or TC^{2-}) due to the loss of protons from the tri-carbonyl system and phenolic di-ketone moiety. The result show that the adsorption then decreases as the pH is increased .that indicate the dominant of cation exchange mechanism of tetracycline's adsorption onto cobalt oxide [18-21].

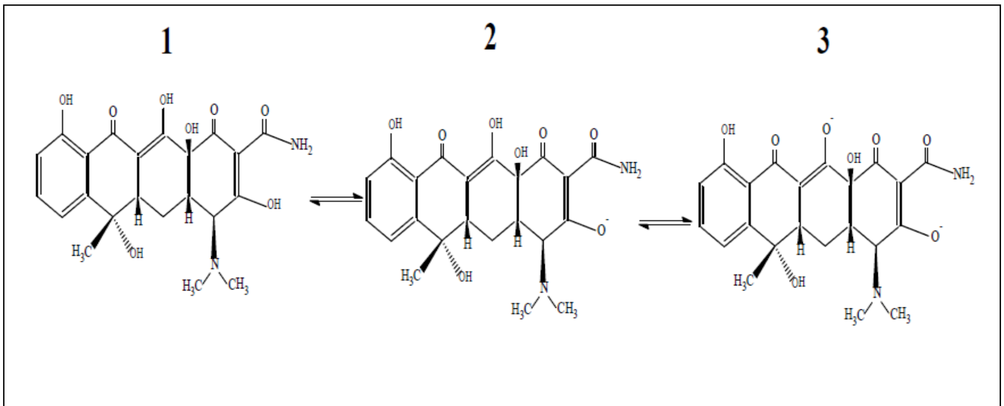

Fig.(7): Increasing of pH caused different forms of the tetracycline.

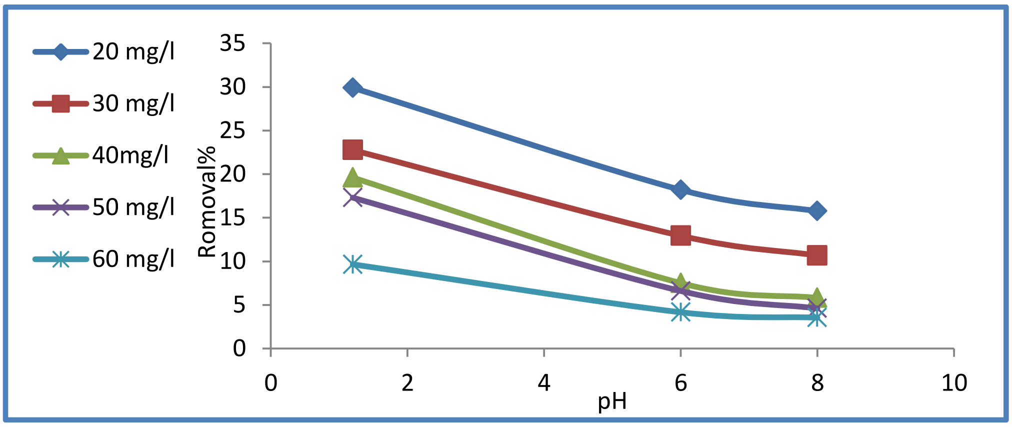

Fig.(8): Effect of pH on tetracycline adsorption at different concentrations.

Point of zero charges (pHzc)

The point of zero charge is the pH at which the adsorbent surface is neutral. The amounts of positive and negative electric charges are equal. Below this value, the surface is positively charged; beyond this value, it is negatively charged [22]. pHzc was determined by the salt addition method. 0.01 gm of Co_3O_4 added to 10 ml volumetric flask containing (50mg/l) of tetracycline were add into 5 flasks in different initial pH (pHi) solutions (1.2, 2.5, 6, 8 and 10). pH values were altered using (0.1 N) of NaOH and HCl, then 0.01 gm of Co_3O_4 was added into all flasks. The pH of solutions was measured after 48 hours, this pH called the final pH (pf). ΔpH=(pHi –pHf) values are plotted against the pHi values PZC value was identified at the pH when Δ pH was zero. [23]. pHzc of Co_3O_4 was determined at pH 7.2 as shown in Fig.(9). So Co_3O_4 had a positively charged at pH < 7.2 and negatively charged at pH > 7.2, the pKa values of the tetracycline molecule were 3.3, 7.7 and 9.27, respectively. Tetracycline occur as cationic in strong acid solution at pH < 3.3, zwitter anions at 3.3 < pH < 7.7 and negative ions at pH >7.7. As is evident, adsorption mechanisms have been given based on pH values were given in Table (4). Positively charge Co_3O_4 < pHpzc < egatively charge Co_3O_4 Table (1) Normally, it is always easier to adsorb a cation on a negatively charged surface, and an anion on a positively charged surface. However, other interactions may be stronger than purely electrostatic forces, making the effect of surface charge not so important. Additionally, a cation is often complexed with ligands, some of them being possibly negatively charged. Therefore, in such a case, the cation is in fact a negative complex, which may adsorb very well on a positively charged surface and that happen in this study. As showed when pH values were low, the cation exchange mechanism between tetracycline cation and positively charged Co_3O_4 was predominant [24-25]. Fig.(10 a and b) is shown the UV-Visible spectra of tetracycline before and after the adsorption process.

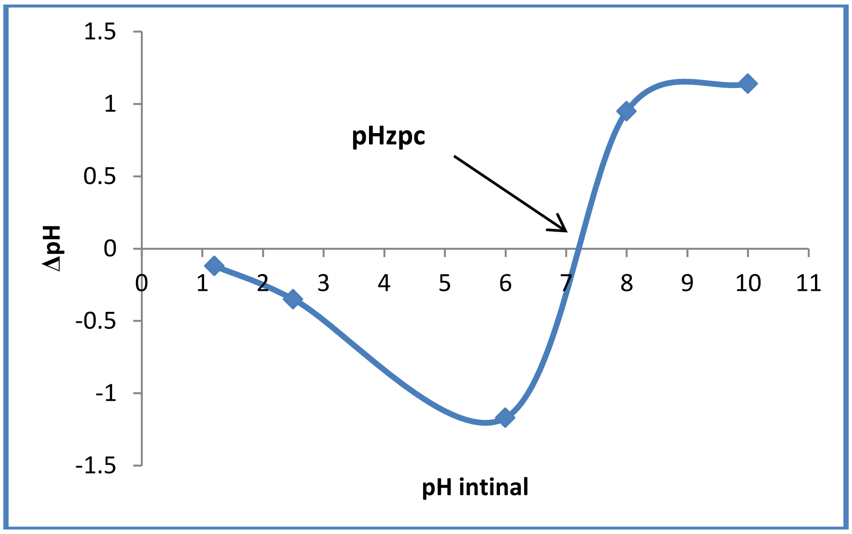

Fig.(9): The point of zero charges of Co_3O_4.

Table (1)
Adsorption mechanisms depending on pH values.

Studied pH range	Adsorption Mechanisms
2.0 < pH < 3.0	Cation exchange
3.0 < pH < 7.0	Cation exchange and surface complexation
pH 8.0	Surface complexation

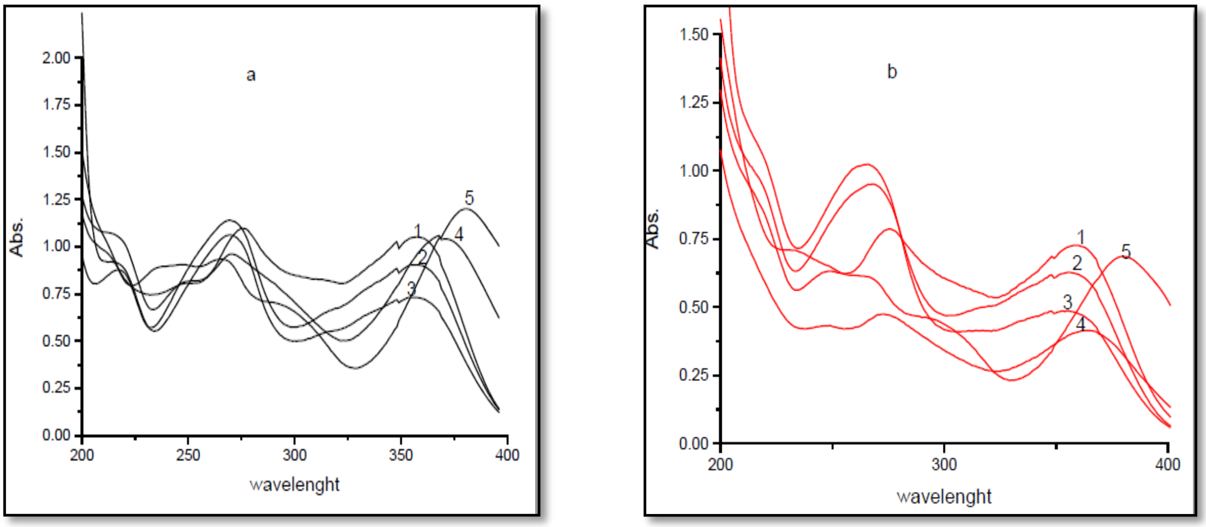

Fig.(10): UV spectra of tetracycline a- before b- after adsorption process (1=pH 6, 2= pH1.5, 3= pH3, 4=pH8 and 5=pH10).

Adsorption isotherm

The equilibrium data isotherm analysis for tetracycline adsorption onto cobalt oxide at various concentrations (20-70 mg/L) and 37 °C, the adsorption data were fitted to the two widely used isotherm models, the Freundlich and Langmuir models.

$$\frac{1}{qe} = \frac{1}{qmKaCe} + \frac{1}{qm} \quad \text{.....................................} (3)$$

$$\text{Log } (q_e) = 1/n \log (C_e) + \log (K_F) \text{.................} (4)$$

C_e is the equilibrium concentration (mg/L), where q_m and q_e (mg/g) are tetracycline uptakes at saturation and equilibrium states, respectively, K_a (L/mg) is the Langmuir constant, KF $mg.g^{-1}(L.mg^{-1})^{1/n}$ and n are Freundlich parameters.

The results confirm the best analysis of isotherm data by the Freundlich isotherm model. Fig.(11) and Table (2) for Freundlich isotherm show a high value for R^2 of (0.99). Values of 1/n (0.88) where the closer value to zero means the more heterogeneous the adsorption surface [27-28].

Table (2)
Parameters for the Langmuir and Freundlich linear isotherm at 37 °C.

isotherm	Constants	parameters
Langmuir	q_a (mg.g^{-1})	0.023
	k_a (Lm.g^{-1})	4.30
	R^2	0.95
Freundlich	n	1.12
	K_F (mg.g^{-1})(Lmg^{-1})$^{1/n}$	4.48
	R^2	0.99

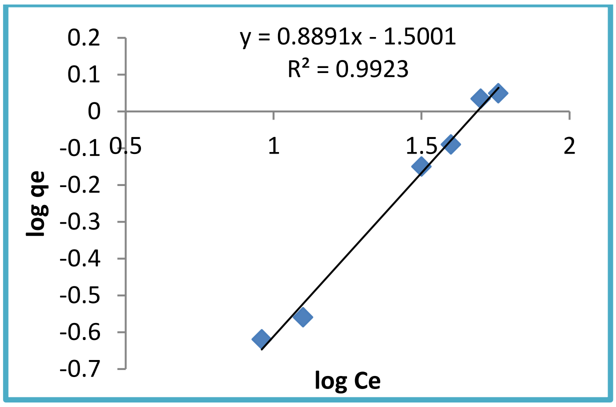

Fig.(11): Langmuir and Freundlich linear isotherm at 37 °C.

Conclusions

This paper shows that cobalt oxide can be used as an efficient adsorbent to remove tetracycline antibiotics from the aqueous solution. The effects of pH, contact time, initial antibiotics concentration, and temperatures on the adsorption capacities have been investigated. Tow isotherm model was studies and the result show that the Freundlich models had the best fitting with data.

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