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RESEARCH ARTICLE

Removal of Pharmaceutical (Paracetamol) by using *CNT/ TiO2* Nanoparticles

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Abstract

Paracetamol has been the highly usage drug in the world which increased environmental pollution, it has been effected in human life, flora and fauna in the world. Adsorption technique was used to remove paracetamol from water using CNT/TiO_2 nanoparticles; the TiO_2 was developed from CNT/TiO_2 nanoparticles. The experiments were carried out to drug uptake by CNT/TiO_2 nanoparticles and effect of some experimental factors like temperature, initial drug concentration, adsorbent dosage, , and particle size in solution, also the adsorption equilibrium was characterized using Langmuir and Freundlich isotherm models. The results have shown immense potential, it was found that correlation coefficient value deal with of the drug, while Langmuir equation was found a good correlation of drug.

Keywords: *Adsorption, Pharmaceutical, Paracetamol, TiO_2, Isotherm models, CNT.*

Introduction

Pharmaceutical (paracetamol) is a drug used in large medicinal and therapeutic strategies it composes of N-acetyl-4-aminophenol (acetaminophen) as a major active component in pharmaceutical preparations. Acetaminophen features characterized as a harsh taste which is usually consists of a hydroxyl, aromatic ring, and amide, also it's a white, odorless and crystalline powder [1, 2] (Fig 1) as a results of antipyretic and analgesic properties of paracetamol drug it's extensively used which causes several problems. It is available by prescription and as an over-the-counter medicine. The main physicochemical properties and the structure of Paracetamol are show in Table 1. The physical and chemical features of the nanoparticles like, multifunctional ,abundant surface active sites, large surface area , and specific affinity were main roles in modern researches [3]. The TiO_2 Nanoparticles have active role in environment purifying and it useful in adsorption phenomena and other applications [4]. Recently pharmaceutical molecules removing from aqueous solutions had a lot of interests in scientific field , a Various adsorbents have been used like activated carbon [5-9], AC/TiO_2 [10], carbon nanotube CNT [11] , aluminum hydroxide, iron-based compounds [12] fly ash [13], Ca-based sorbents [14]. The adsorption considered one of the an effective approaches according to its easily–handle operation for molecules removing, however several researches considered it as a competitive method due to low cost, and eco-friendly characters [15-17]. The goal of this study was to evaluate the efficacy of CNT decorated TiO_2 and adsorbent to remove paracetamol drug from solutions. In addition to study some parameters effects included initial drug concentration, adsorbent dose, and temperature. The adsorption isotherms also analyzed.

Fig1: Paracetamol Chemical structure

Table1: Chemical and physical properties of paracetamol

IUPAC ID	N-(4-hydroxyphenyl) ethanamide, N-(4-hydroxyphenyl)acetamide
Chemical term	Acetaminophen; 4-Acetamidophenol; Paracetamol
Molecular Formula	$C_8H_9NO_2$ or $HOC_6H_4NHCOCH_3$
Boiling point	420 °C (788 °F)
Density g/cm^3	1.263
Melting point	169 °C (336 °F)
Molecular Weight (g mol $^{-1}$)	151.2
pKa	9.38
So. H_2O (25 ^oC mg mL^{-1})	14
LogP	0.46

Experimental

Materials and Methods

A stock solution (100 mgL^{-1}) of the preparing of CNT/TiO_2 nanoparticles by mixing (0.5 g) as an appropriate quantity of Pharmaceutical drug in (500ml) distilled water, then Working and standards (10–100 mgL^{-1}) solutions made of using successive dilutions from stock solution in dH_2O. Spectrophotometric analysis was done to estimate absorbance by UV-Visible Spectrophotometer (Fig 2).

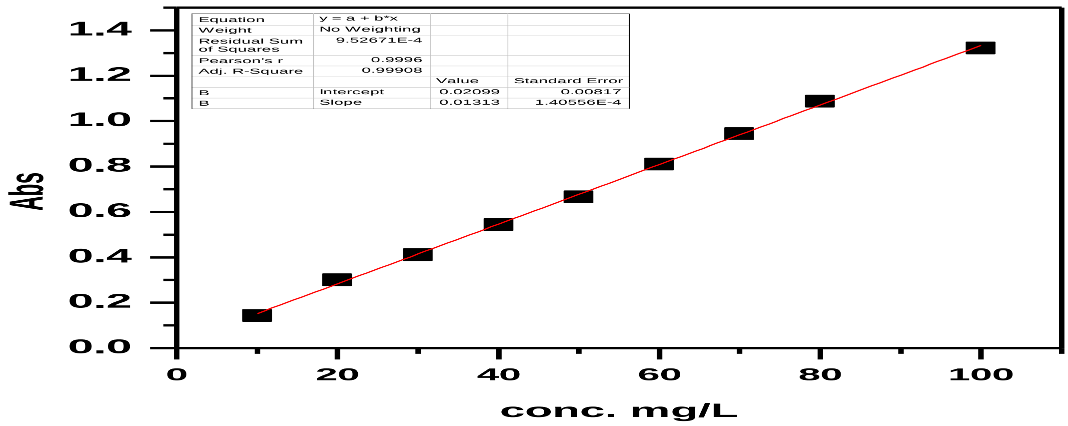

FIG. 2: STANDARD CURVE OF PARACETAMOL DRUG

CNT-loaded TiO_2 Preparation

Were supplied from our lab in college of science for women-Chemistry Department-University of Babylon, already prepared in our previous published article [18].

Different Parameters Effect in Adsorption Process

Particle Size

Particle size effect in the CNT/TiO_2 nanoparticles adsorption capacity was performed in (50, 75, and 100 mm), at 25 ^{0}C, 130 rpm, Ph 6, 0.05 g of CNT/TiO_2 nanoparticles and 100 mL of drug concentration 30 mgl^{-1}.

Initial Drug Concentration

Drugs Initial tested concentrations were 10, 20, 30, 40, 50, 60 70, 80 and 100 mg/L of drug onto (CNT/TiO_2 nanoparticles) with shaking in water-bath at 25 °C.

Mass Dosage

The adsorption dosage effect implemented by diverse masses (0.01, 0.05, 0.075 and 0.1) g agitating with CNT/TiO_2 nanoparticles (size 50 µm) in 100 mL of drug has concentration (30 mg.L^{-1}) with shaking by shaker water -bath at 25 °C. in pH 6. Agitation for 24hr at 130 rpm.

Solution Temperature

It determined by agitating (24hr and speed 130 rpm) of different solution temperatures included (10, 25, 35 and 60 ^{o}C), mass con was 50 mg of CNT/TiO_2 nanoparticles in 100 mL of drug con. (30 mg.L^{-1}) by water-bath shaker at PH 6.

Adsorption equilibrium Determination

It was carried out by agitating of 100 mL drug solutions of known initial concentration with adsorbent (30 mg/L of) at tm 25^{o}C, pH of 6.0± 0.2 with 130 rpm for different times.

A amount of drug adsorbed onto the adsorbent at equilibrium, qe (mg/g), was calculated according to equation:

$$E\% = (C_0 - C_e) / C_0 * 100 \quad (1)$$

$$Q_e = (C_0 - C_e) * V / W \quad (2)$$

C_0 initial con.(Mg/L) V volume of solution (L), C_e equilibrium drug con (mg/L), , and W adsorbent mass (gm).

Results and Discussion

Effect of First Parameters Drug Concentration

The initial drug con. Play important rule in the quantity of adsorption. The obtainable sites in surface of absorbance correlated directly with the initial concentration of drug Fig. 3 clarified the outcome of initial drug concentration on parameters removal by CNT/TiO_2 nanoparticles, also the amount of drug elimination decreased with elevated in initial parameters concentration, while, drug adsorbed per unit mass of CNT/TiO_2 nanoparticles (Co) increased with initial parameters concentration increments.

Figure 3 shows that the qe/mg.g^{-1} value improved with the elevation in initial parameters concentration as the resistance to the acceptance of drug from the solution reduced with the elevated in parameters concentration. Also, the increasing of Co amount would leads to an increase in the rate of adsorption due to the arising in the driving force [12, 14, 19].

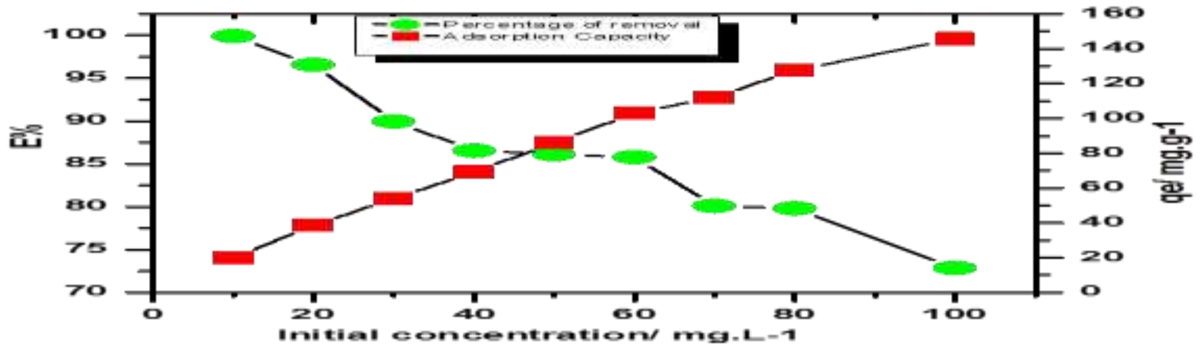

Fig. 3: initial adsorbent dosage effects in Paracetamol drug adsorption using CNT/TiO_2 nanoparticles surface (mass dosage 0.5 g/L, 25 °C and pH 6)

Effect of CNT/TiO_2 Mass Dosage

The research work has been done to investigate the effect of CNT/TiO_2 nanoparticles amount in the drug elimination (adsorption) at 25 ±1 °C. Fig. 4 shows that the percentage elimination of drug raised up with an increase in the CNT/TiO_2 nanoparticles dose (0.01–0.1 gm). The increase in surface area of CNT/TiO_2 may be the reason of elevation in the drug removal as a more effective site were be obtainable for adsorption [20].The efficiency of drug abstraction was 97% at the optimum dose of CNT/TiO_2 nanoparticles, Also the results of increment of adsorbed drug quantity. The adsorption concentration reduction with adsorbent amount elevation is mostly because through reaction sites number was available for elevated adsorption site by adsorbent amount increment while adsorption sites remain unsaturated [9, 21].

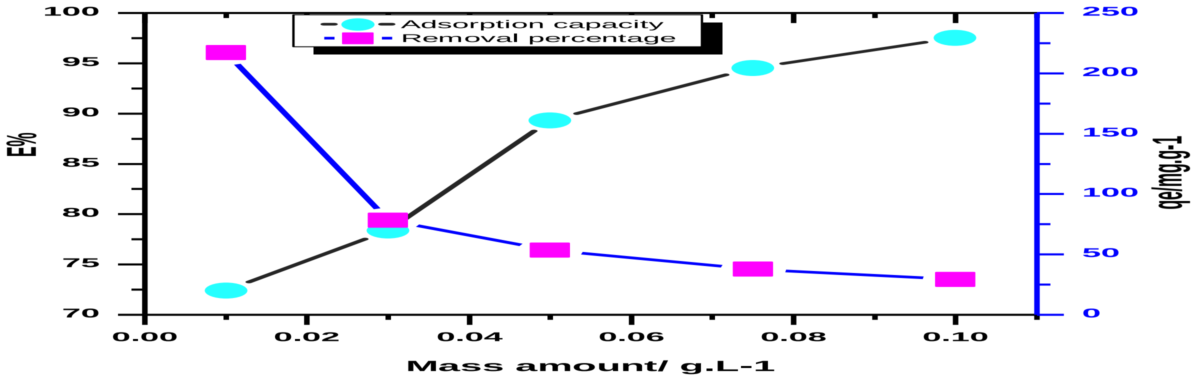

Figure 4: CNT/TiO_2 nanoparticles surface concentration effect on Paracetamol drug Experiment conditions: pH 6, 25 °C and initial conc. 30mg/L)

Particle Size Effectiveness

The drug adsorption capacity was highly affected by particle size of an adsorbent. Two criteria would manage the relationship between the adsorption capacity and particle size: firstly, adsorbent intrinsic characteristic included porosity, rigidity of the polymeric chains and crystallinity. Secondly, ionic charge of the drug molecule (chemical structure) and its ability to form hydrolyzed species [22]. Fig. 5 explained particle size effect in drug adsorption. The smallest particle size had larger adsorption capacity than large particle size. would be a good evidence drug favorably adsorbed on the outer surface and cannot entrance totally in the spaces between particles resulting from steric hindrance of big drug molecules [23].

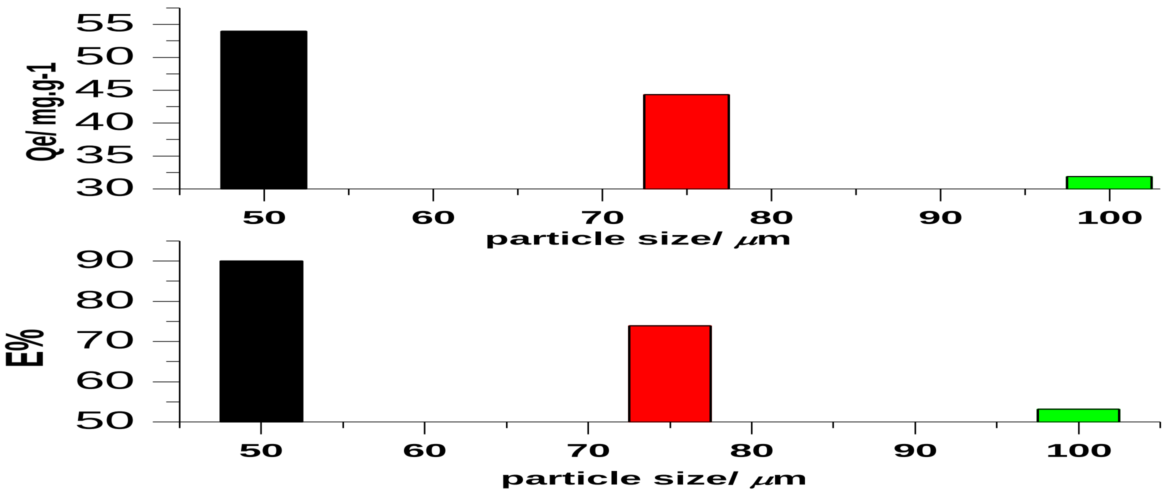

Fig.5: particle size effectiveness in amount of adsorbed Paracetamol drug and removal percentage onto CNT/TiO_2 nanoparticles at pH 6, 25 °C, mass dosage 0.5 g/L, and initial conc. 30mg/L

Effect of Temperature

The effect of different Tm has been detected in present study , research improved that T increasing of the adsorption medium causes reduced in aqueous solution viscosity, also the rate of diffusion of the adsorbent molecules over the external margin layer and in the adsorbent particles internal pores [24, 25]. Therefore, present study aims to determine the temperature effect in the adsorption rate of the drug onto CNT/TiO_2; this was achieved in arising the temperature (10, 25, 35 and 60°C) with adsorption quantity. The adsorption capacity for drug initial concentration 30 mgL^{-1} elevated from 32.391mg·g^{-1} (55.944% removal) to 59.996 mg·g^{-1} (99.979% removal) with temperature increment (10 - 60°C), results improved that the adsorption process of drug cations was endothermic in nature (Fig 6).

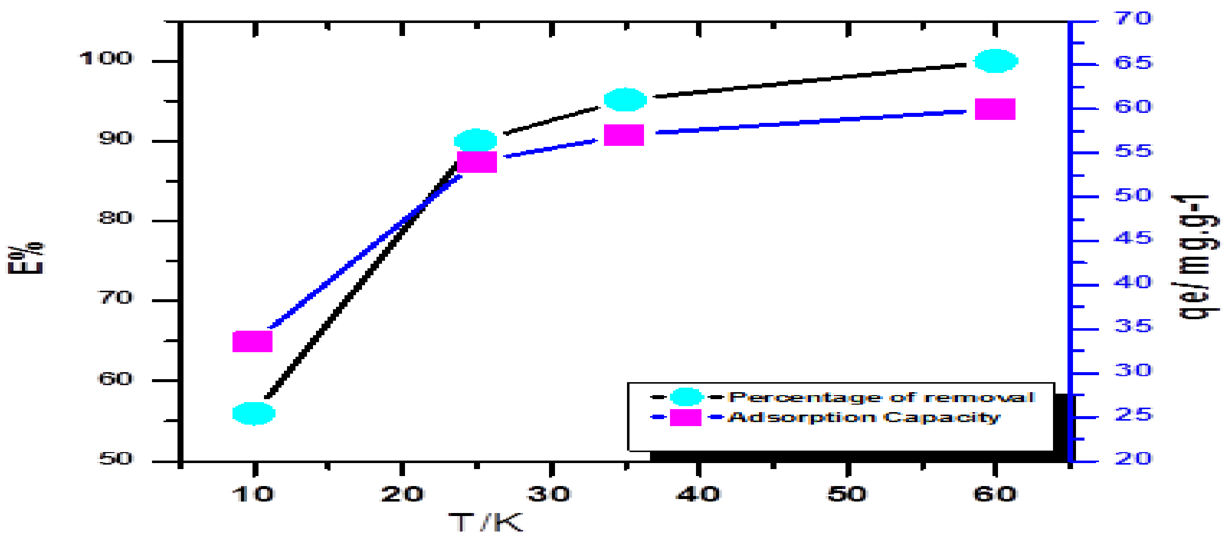

Fig. 6: solution temperature effectiveness in Paracetamol drug adsorption by *CNT/ TiO_2* nanoparticles surface percentage of removal, and adsorption capacity (mass dosage 0.5 g/L and initial conc. 30mg/L. at pH 6).

Models of Adsorption Isotherms

Freundlich Isotherm

The Freundlich isotherm is known as equation 3 [26, 27].

$$q_e = K_f C_e^{1/n} \quad 3$$

Qe: adsorbent Amount adsorbed / unit weight at equilibrium (mg/g), (mol/g), C_e: the adsorbate Equilibrium con in solution after adsorption (mg/L), (mol/L) ,K_f : capacity factor ($L.g^{-1}$) , 1/n heterogeneity factor , n is a deviation measured of the deviation from adsorption linearity. Its value indicates non-linearity degree between adsorption and solution concentration as follows: adsorption route is chemical if value under to unity or it is linear if the n value equal to unity, finally the favorable physical route when value is above unity adsorption [28].A plot of q_e versus Ce (Fig.6) where the values of K_F and 1/n are optained from the intercept and slope of the linear regressions (Table 2).

Langmuir Isotherm

It is used for the adsorption of pollutants from liquid solutions [29, 30]. Langmuir derived other equation on the definite case of the adsorption rout nature from solution. The Langmuir adsorption isotherm was developed based that [31] All accessible sites fixed number has same energy and it is available on the adsorbent surface, There was reversible Adsorption.Occurring of Monolayer adsorption.**And** no lateral interactions among the adsorbates. thus Langmuir adsorption isotherm is clarified in equation 4 [29, 30]

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad 4$$

Where q_e: adsorbed amount per unit weight at equilibrium (mg/g), C_e: con. Of adsorbent equilibrium in solution after adsorption (mg/L), q_m: the constant of Empirical Langmuir represents maximum adsorption capacity (mg/g), K_L: empirical Langmuir constant (L/mg). The Results of this model are shown in Figures (6), and the Langmuir constants are illustrated in Tables (2).

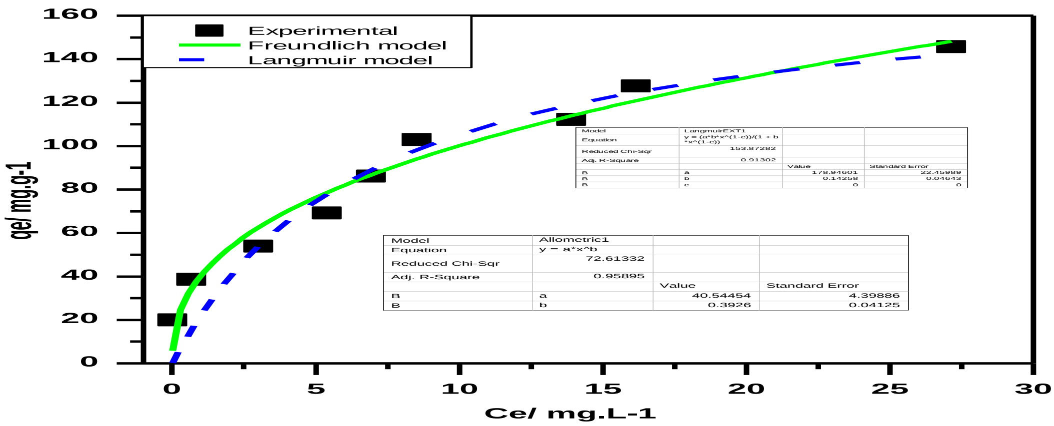

Fig.8: Paracetamol drug adsorption model of Different adsorption isotherm nonlinear fit . on *CNT/TiO₂ nanoparticles* at pH 6, mass dosage 0.5 g/L, 25 °C initial conc. 30mg/L

Table 2: Model of Langmuir and Freundlich, isotherms parameters for Paracetamol drug adsorbed on the surface of CNT/TiO_2 nanoparticles at 25 °C

Isotherm models	Parameters	Paracetamol drug
Langmuir	qm ($mg.g^{-1}$)	178.946 ± 22.45
	K_L($L.mg^{-1}$)	0.1425 ± 0.046
	R^2	0.913
Freundlich	K_F	40.5445 ± 0.398812
	1/n	0.392 ± 0.0412
	R^2	0.9589

Conclusions

The present study concluded that the using CNT/TiO_2 nanoparticles source as an alternative adsorbent surface for elimination of pharmaceutical (Paracetamol drug) was so effective. The Model classification due to the adsorption isotherms simulation is: Freundlich > Langmuir. Also the minimum particle size revealed larger adsorption capacity than the bigger particle size. In another word, the elevation in adsorption capacity proportional with reducing particle size.

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