Ultrasound-assisted adsorption of pharmaceuticals onto clay decorated carbon Nano composites as a novel adsorbent: as a Applicable for environmental studies

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Abstract

Pharmaceutical pollutants substantially affect the environment; thus, their treatments have been the focus of many studies. Pharmaceuticals, which are frequently detected in natural and wastewater bodies as well as drinking water have attracted considerable attention, because they do not readily biodegrade and may persist and remain toxic. As a result, pharmaceutical residues pose ongoing and potential health and environmental risks. To tackle these emerging contaminants using one type of Carbon source (CNT) has been widely used as highly effective adsorbent for antibiotics because of its large specific surface area, high porosity, and favorable pore size distribution. In this study, the adsorption performance of CNT towards major types of antibiotics such as Phenylephrine hydrochloride drug. The removal present increase with increase amount of adsorbent but decrease with increase initial drug concentration, and contact time. The equilibrium data were evaluated using Langmuir, Freundlich isotherms. Freundlich, model best describes the uptake of drug.

Keywords: Pharmaceuticals, Phenylephrine hydrochloride drug, Nanocomposites, Adsorption, Ultrasound, Clay.

Introduction

The pollution produced by pharmaceutical products in surface and ground waters has been acknowledged by many countries as an environmental problem and has led to the establishment of a research field known as Pharmaceuticals in the Environment. The pharmaceutical industry uses the designation Active Pharmaceutical Ingredients to describe products that are pharmacologically active, resistant to degradation, highly persistent in aqueous medium, and potentially able to produce adverse events in water
organisms and have a negative impact on human health.\[1\]

Therapeutic groups most commonly detected in water are: (i) anti-inflammatory drugs and analgesics (paracetamol, acetylsalicylic acid, ibuprofen, and diclofenac); (ii) antidepressants (benzodiazepines); (iii) Antiepileptics (carbamazepine); (iv) lipid-lowering drugs (fibrates); (v) β-blockers (atenolol, propanolol, and metoprolol); (vi) antiulcer drugs and antihistamines (ranitidine and famotidine); (vii) antibiotics (tetracyclines, macrolides, β-lactams, penicillins, quinolones, sulfonamides, fluoroquinolones, chloramphenicol and imidazole derivatives); (viii) other substances (cocaine, barbiturates, methadone, amphetamines, opiates, heroin, and other narcotics) \[1,2\]. Several methods to remove pharmaceutical products, including biodegradation\[3\], electrocoagulation \[4\], ozonation \[5, 6\], ultrafiltration membrane \[7\], and adsorption\[8\], have been used to treat pharmaceuticals. Among these methods, adsorption is the simplest, cheapest, and most versatile technique for holding these pollutants \[9\], Activated carbon \[10\], biochar \[11\], mesoporous silica \[12\], zeolite \[13\], chitosan \[14, 15\], carbon nanotubes (CNTs) \[16\], clays \[17\], resin \[18\], biomass wastes \[18, 19\], and graphene oxide \[20\] adsorbents have been effectively utilized to attract pharmaceutical pollutants from wastewaters.

**Experimental Part**

**Adsorption experiments**

For Phenylephrine hydrochloride drug removal from aqueous solution, typical adsorption experiments were performed to evaluate and compare the capacity of CNT /Decorated / Clay(Bentonite) / Fe2O3 Micro/Nanocomposites. PHE stock solutions (1000mgL\(^{-1}\)) were prepared with detail water and all subsequent experiments were made by diluting these solutions. The experiments were carried out in a Sonication water bath using Erlenmeyer flasks and, the experimental conditions were determined by preliminary tests. For all experiments the volume of solution was 100 mL. Firstly, the adsorbent dosage effect was investigated from 0.01 to 0.15 g L\(^{-1}\), at the original solution pH (6), temperature of 298 K, agitation of 3000 rpm, contact time of 1 h and initial concentration of 50 mg L\(^{-1}\). The effect of pH solution was studied by agitating 0.1 g of CNT /Decorated / Clay(Bentonite) / Fe2O3 Micro/Nanocomposites and 100 mL of PHE drug concentration (50 mgL\(^{-1}\)) using Sonication water-bath at 25°C. The experiment was conducted at different pH from 3, 6, 8, 11. Agitation was provided for 1 h contact time at a constant agitation speed. The pH was adjusted by adding a few drops of diluted 0.1 N KOH, or 0.1 N HCl and measured by using a pH meter. Then, equilibrium isotherms were obtained at temperatures (298 K) with PHE drug concentration range from 2 to 100 mg L\(^{-1}\), CNT /Decorated / Clay(Bentonite) / Fe2O3 Micro/Nanocomposites and 100 mL of PHE drug concentration (50 mgL\(^{-1}\)) using Sonication water-bath at 25°C. The experiment was conducted at different pH from 3 ,6,8, 11. Agitation was provided for 1 h contact time at a constant agitation speed. The pH was adjusted by adding a few drops of diluted 0.1 N KOH, or 0.1 N HCl and measured by using a pH meter. Then, equilibrium isotherms were obtained at temperatures (298 K) with PHE drug concentration range from 2 to 100 mg L\(^{-1}\), CNT /Decorated / Clay(Bentonite) / Fe2O3 Micro/Nanocomposites. dosage of 0.1 g L\(^{-1}\) and pH of 6.5. In this case, the solutions were stirred at 3000 rpm until the equilibrium. Finally For all experiments, samples were collected, centrifuged at 3000 rpm for 10 min, and the remaining PHE concentration in liquid phase was determined by spectrophotometry at the maximum wavelength of absorption (272nm) using a spectrophotometer. The experiments were carried out in triplicates and blanks were performed. The dye removal percentage (%R), equilibrium adsorption capacity (q\(_{e}\)) were determined by Eqs. (1)–(2), respectively:
\[ E\% = \frac{C^0 - C_e}{C^0} \times 100 \quad (1) \]

\[ Q_e = \frac{(C^0 - C_e) \cdot V}{W} \quad (2) \]

where \( C^0 \) is the initial dyes concentration in liquid (mg L\(^{-1}\)), \( C_e \) is the equilibrium dyes concentration in liquid (mg L\(^{-1}\)), \( m \) is the amount of adsorbent (g) and \( V \) is the volume of solution (L)

**Result and Dictation**

**Characterization of The Preparation CNT /Decorated /Clay(Bentonite) / Fe\(_2\)O\(_3\) Micro/Nanocomposites**

Energy Dispersion X-ray

EDX is a versatile technique used for qualitative and semi-quantitative analysis, it was noted that the iron in the clay(Bentonite) was increased in the presence of carbon and Fe2O3 impetration. For pristine clay(Bentonite), it showed larger particle size and unequal particles due to stacking of flaky materials in comparison to the treatment with hydrochloric acid and sodium chloride where these particles were disaggregated to smaller flakes and a clear microstructures difference distinction (Figures 1).

Morphology and Microstructure Analysis

The samples appeared with crapy, rough and porous fracture surface (Figure 3). This increase the surfaces of the absorbents that facilitates water diffusion into the absorbent.
At magnification over 1000X, bentonite clay/CNT lamellar structures were clearly visible (Figure 3). Furthermore TEM provide good agreements with the results of SEM[21, 22].

Figure (3): SEM images of CNT/Clay(Bentonite) /Fe$_2$O$_3$.

**Transmittance Electron Microscopy (TEM)**

Transmittance electron microscopy is a suitable technique for studying the surface morphology, results show good agreement with the FESEM measurements shown in Figure (4).

Figure (4): TEM image for CNT decorated Clay(Bentonite) /Fe2O3
Chemical Composition (XRF) Analysis

XRF analysis consider a very important technique for determination percentage of oxide in a mixture, results are shown in Tables (1). An evident increase in Fe$_2$O$_3$ content indicates Fe species had been loaded on bentonite for all sample were decorated by C substrate, the highest value of Fe$_2$O$_3$ (11.77 %) percentage is shown in Table (2) this attributed to exist of a higher percentage if the pristine of CNT sample [23].

Table (1): XRF analysis of Bentonite Clay

|            | 524-4 | L.O.I. | MgO | Al2O3 | SiO2 | P2O5 | SO3 | Cl |
|------------|-------|--------|-----|-------|------|------|-----|----|
| (%)        | 81.97 | 0.033  | 0.99 | 16.379| 0.026| 0.351| 0.046|

|            |            | K2O | CaO | Fe2O3 | Ni  | Zn  |
|------------|------------|-----|-----|-------|-----|-----|
| Traces:    |            |     |     |       |     |     |
|            |            | 0.099| 0.188| 0.755 | 0.007| 0.048|

Table (2): XRF analysis of CNT decorated/Bentonite clay supported Fe$_2$O$_3$

|            | 524-1 | L.O.I. | Na2O | MgO  | Al2O3 | SiO2  | P2O5 | SO3 | Cl |
|------------|-------|--------|------|------|-------|-------|------|-----|----|
| (%)        | 20.48 | 0.07   | 3.847| 11.164| 43.117| 0.661 | 0.812|

|            |            | K2O | CaO | TiO2 | Cr  | MnO | Fe2O3 | Ni  |
|------------|------------|-----|-----|------|-----|-----|-------|-----|
| Traces:    |            |     |     |      |     |     |       |     |
|            |            | 0.017| 0.408| 7.005 | 0.62 | 0.021| 0.036 | 11.77| 0.008|

|            |            | Cu  | Zn  | Sr   | Zr  | Mo  |
|------------|------------|-----|-----|------|-----|-----|
| Traces:    |            |     |     |      |     |     |
|            |            | 0.012| 0.099| 0.009| 0.007| 0.007|

Effect of Weight of Composite

Variation of adsorbent dose showed that although increasing of weight of composite in aqueous solution can result to increased drug removal. The plot of removal % of PHE drug adsorption against the weight of CNT /Decorated /Clay(Bentonite)/Fe2O3 Micro/Nanocomposites adsorbent respectively in gram. From the Figures 5 it is observed that the percentage of adsorption is increases with increase in the adsorbent. This can be attributed to an increase in surface area of the nanocomposites, which in turn increases the binding sites. At higher dosage, there is
a very fast adsorption on to the adsorbent surface that leads to improved uptake of the drug [24-26].

![Graph showing effect of mass amount of adsorbent on percent removal and amount of adsorbed PHE drug](image)

Figure(5): Effect of mass amount of adsorbent (Clay(Bentonite) /CNT) nanoparticles on the percent removal and amount of adsorbed PHE drug, initial concentration = 50 mg/L, Temp. = 25°C, contact time 1 h.

**Effect of pH**

pH Solution can play an important role for the adsorption of the analytics by affecting both the existing forms of the target compounds, the charge species and density on the sorbent surface. In this work, the effect of pH solution on the extraction of target is investigated in the pH range of 2.0-11.0. As can be seen from Figure (6) , the sorption percentage of drug on CNT /Decorated /Clay(Bentonite)/Fe2O3 Micro/Nanocomposites very little in pH range of 2-4, which suggests that CNT /Decorated /Clay(Bentonite)/Fe2O3 Micro/Nanocomposites are excellent adsorbents for drug removal from large volumes of aqueous solutions. The results show a maximum adsorption of PHE pH 6. At pH .above 8, the amount of PHE drug noticeably decreases following a typical anionic adsorption behavior. [27-29].
Figure (6): Effect of solution pH on the adsorption of PHE drug on clay(Bentonite)/CNT. (Exp. Condition: Temp. = 25°C, contact time 1 h, and pH of solution 6).

The initial drug concentration effect

Different concentrations of PHE drug 2-100 mg/L were selected. The amounts of drug adsorbed at pH 6, adsorbent dosage 0.1g and 25°C are given in Figure 7. With increasing initial concentration of PHE drug from 2 to 100mg/L, the removal of drug molecules decreases from 99.47 to 81.59% after 1 hr of equilibrium adsorption time [26, 30, 31].

Figure(7): Effect of initial concentration on the percent removal and amount of adsorbed PHE drug onto Clay(Bentonite) /CNT (Exp. Condition: Temp. = 25°C, contact time 1 h, and pH of solution 6).
Adsorption isotherms

Two isotherm models namely Langmuir and Freundlich isotherm were examined. Linear regression was used to determine the best fitting model. The Langmuir model supposes that adsorption occurs uniformly on the active sites of the adsorbent surface. Once the adsorbate occupies an active site, no further adsorption can take place at this site. The Langmuir adsorption equation is[32]

\[ Q_e = q_m \frac{K_L C_e}{1+(K_L C_e)} \]  

Where, \( q_e \) is the amount adsorbed (mg/g) at equilibrium. \( C_e \) is the equilibrium solution concentration (mg/L). \( Q_0 \) and \( b \), the Langmuir constants represent the maximum adsorption capacity (mg/g) at complete monolayer coverage and energy of adsorption respectively. [33]

Where \( C^0 \) is the initial dyes concentration and \( b \) is the Langmuir constant. This parameter can indicate whether the adsorption process is irreversible (\( RL = 0 \)), favorable (\( 0 < RL < 1 \)), linear (\( RL = 1 \)) or unfavorable (\( RL > 1 \)) Freundlich Isotherm model is defined as:[34]

\[ Q_e = K_F C_e^{1/n} \]  

where \( q_e \) is the amount adsorbed (mg/g), \( C_e \) is the equilibrium concentration of dyes solution (mg/L). \( K_F \) (mg/g) represents adsorption capacity and \( n \) is the dimensionless exponent of the Freundlich equation representing adsorption intensity.

A plot of \( q_e \) versus \( C_e \) (Figure 8) where the values of \( KF \) and \( 1/n \) are obtained from the intercept and slope of the linear regressions (Table 3).
Figure (8): Nonlinear fit of different adsorption isotherm models for adsorption of PHE drug on (clay(Bentonite) /CNT), initial concentration = 50 mg/L, Temp. = 25°C, contact time 1 h, and mass of adsorbent 0.1 g/L.

Table (3): Langmuir and Freundlich, model isotherms parameters for PHE drugs adsorbed on the surface of (clay(Bentonite) /CNT) at 25 °C.

| Phenylephrine hydrochloride | Parameters | Clay/CNT |
|-----------------------------|------------|----------|
| Isotherm models             |            |          |
| Langmuir                    | qm (mg/g)  | 0.2791±0.07476 |
|                            | KL(L/mg)   | 87.1358±8.3875  |
|                            | R²         | 0.95229  |
| Freundlich                  | Kᵢ         | 0.40561±0.0121 |
|                            | 1/n        | 2.37058±0.6821 |
|                            | R²         | 0.9966  |
Conclusions

The results of EDX analysis shows that the elemental contents of Clay(Bentonite)/CNT were mainly composed of C, Fe and O elements. Highly removal of PHE drug in the presence of Clay(Bentonite)/CNT nanocomposites the removal of drug molecules decreases from 99.47 to 81.59% after 1 hr of equilibrium adsorption time and the percentage of adsorption is increases with increase in the adsorbent.

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