A comparative between sonication and adsorption technique to removal Pharmaceuticals pollutant

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Abstract
Synthesis of C deposits/Clay/Fe2O3 as a new Micro/Nanocomposite adsorbent for removal of pollutants (Amoxicillin (AMX), Phenylephrine Hydrochloride (PHE)) from aqueous solutions. Micro/Nanocomposites are synthesized by using the hydrothermal method, and loaded with type of carbon (C) on Clay surface. A Comparative study between (commercial Sugar (Sucrose) / Clay (Bentonite) / Fe2O3 Micro / Nanocomposite, CNT / Clay (Bentonite) / Fe2O3 Micro / Nanocomposite, AC/Clay(Bentonite)/Fe2O3 Micro/Nanocomposite, that found CNT, AC and Clay (Bentonite) the best result to removal pollutant found CNT / Clay (Bentonite) /Fe2O3Micro /Nanocomposite gave E% (93.11 %) of PHE and (81.11%) of AMX at optimized value of agitation time is 60 min after that the adsorption becomes constant.

Key word: Pharmaceutical, Adsorption, Removal, Nanomaterial, Clay (Bentonite).

1. Introduction

Adsorption is a rapid phenomenon of passive sequestration separation of adsorbate from an aqueous/gaseous phase on to a solid phase [1-4]. Adsorption occurs among two phases in transporting contaminants from one phase to another. It is considered to be a compound phenomenon and depends mostly on the surface chemistry or the nature of the adsorbent, adsorbate and the method conditions in among the two phases [5-7]. The term "nanomaterial" is indicated to as the broad spectrum of substances whose particles possess 1 or 2 dimensions, subject to a nanometer ranging from 1-100 nanometers. Where the nanoscale is approximately 1,000 times lesser than the micrometer [8-10]. Nanomaterials are the bridge connects the atoms and micro-structures. Nanomaterials are much closer to dimensions close to atomic dimensions. For comparison, the length bond between ordinary carbon atoms, or the spacing between these atoms in the molecule, is in the range 0.15-0.12 nm [1, 11, 12]. The properties of nanomaterial are influenced by some of their particle properties for example the shape, size and chemical structure of their particles, which can vary depending to the way they are prepared. The difference is because of nanomaterials have excellent features can be used in unique applications [13-
There was considerable variation in the features of the nanostructures of the same materials from their microstructures, such as chemical, electrical, spectral, magnetic, and many other properties.

2. Experimental Part

Preparation of C Decorated (commercial Sugar (Sucrose); AC; CNT)/Clay (Bentonite) / Fe$_2$O$_3$ Micro/Nanocomposite

Nanocomposite (C decorated/Clay (Bentonite) supported by Fe$_2$O$_3$) were prepared by using hydrothermal process (Scheme (1)). 5 g of clay (Bentonite) and 0.3g of CNT; 0.5g AC; and 1g of commercial Sugar (Sucrose) were mixed. The mixture was added to basic solution of FeCl$_3$ (0.2 mol/L). then complete to 100mL with distilled water then mixed for 1hr to get slurry solution. The resultant mixtures were kept at 160°C for 24 hr. in an autoclave. The obtained dark brown precipitate was filtered, washed with distilled water and ethanol then sonicated in 10 min. intervals then dried at 80°C for 24 hr. to get a fine powder.

Scheme (1): Preparation of C decorated (commercial Sugar (Sucrose); AC; CNT) Clay (Bentonite) / Fe$_2$O$_3$ Micro/Nanocomposite

Determinations of optimum wavelengths ($\lambda_{\text{max}}$) and Calibration Curves of Drugs

To determine the wavelength for maximum absorbance of the PHE and AMX drugs, the ultraviolet-visible absorption spectrum of drugs solution (100mg/L) was recorded within wavelengths of 200-400nm. Where the wavelength for maximum absorbance of the drugs solution was determined from its highest absorption in the UV-Vis spectrum found at the wavelength $\lambda_{\text{max}}$ AMX = 279nm) and $\lambda_{\text{max}}$ PHE = 272nm as shown in (Figure 1).
Figure (1): Absorption spectra of (—) 100mg/L of phenylephrine HCl, (—) 100mg/L amoxicillin and (—) a mixture of 100mg/L of both drugs.

The calibration curve of different concentration of each drug were prepared in serial dilutions (2-100 mg/L). Absorbance was measured at the $\lambda_{\text{max}}$ for each drug and plotted against the concentration values of AMX and PHE (Figure2).

Figure (2): Calibration curve for Phenylephrine hydrochloride (PHE) and Amoxicillin (AMX)

Table (1): Statistics data of calibration for different concentrations of Phenylephrine hydrochloride and Amoxicillin (AMX).

| Parameters          | Proposed Method (AMX) | Proposed Method (PHE) |
|---------------------|------------------------|------------------------|
| $\lambda_{\text{max}}$ (nm) | 279                    | 272                    |
| Beer’s law limit (µg/ml)   | 2-100                  | 2–100                  |
| Regression equation     | $Y = 0.00328X + 0.00138$ | $Y=0.009X-0.0204$     |
Slope (m) | 0.00328 | 0.0090 |
Intercept (C) | 0.00138 | -0.0204 |
Correlation coefficient (r²) | 0.997 | 0.9988 |
Color | Colorless | Colorless |

3. Result and Dictation

Characterization of The Preparation C / Decorated / (Bentonite) Clay / Fe₂O₃ Micro/Nanocomposites

X-Ray Diffraction (XRD)

X-ray diffraction was measured to study the crystal phases and the purity components of nanomaterials. It gives detailed information about the lattice parameter, lattice defects, lattice strain, crystallite size (in case of nanoparticles) and the type of molecular bond of crystalline phase. Therefore, for estimation of the average size of the particles using Sheerer equation \(^1\)

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

Where: D: average particle size, k: shape factor (0.9), λ: wavelength (0.15418nm for Cu-Kα), β: diffraction peak full width at half maximum (FWHM) at 2θ (that is broad due to the crystallite dimensions), θ: angle at maximum diffraction curve intensity.

Figure (3) shows the X-ray diffraction pattern of the AC/Clay (Bentonite) supported by Fe₂O₃; CNT / Clay (Bentonite) supported by Fe₂O₃ and commercial Sugar (Sucrose) / Clay (Bentonite) supported by Fe₂O₃ respectively. Result show, all patterns are mostly semi-similar; There are no diffracted signals of the CNT, AC or commercial Sugar (Sucrose) as a source of Carbon, which attributed to the low weight percentage or non-crystallinity of doping materials on the crystal surface (From Sheerer results 289.7; 245.69; and 211.56 nm for AC decorated clay(Bentonite); commercial Sugar (Sucrose) decorated clay(Bentonite) and CNTs decorated clay (Bentonite) respectively).

Figure (3): XRD of Prepared C /decorated /Clay (Bentonite) / Fe₂O₃ Micro/Nanomaterials
analysis of XRF consider a so significant method for determination of oxide percentage in a mixture, data are appear in Tables (2). An evident rise in Fe$_2$O$_3$ content indicates Fe species had been loaded on bentonite for wholly sample were decorated via C substrate, the highest value of Fe$_2$O$_3$ (11.77 %) percentage is appear in Table (2) this attributed to exist of a higher percentage if the pristine of CNT sample [18].

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

|   | NaO | MgO | AI2O3 | SiO2 | P2O5 | SO3 |
|---|-----|-----|-------|------|------|-----|
| (%) | 20.48 | 0.07 | 3.847 | 11.194 | 43.117 | 0.661 |
| Cl | 0.017 | 0.408 | 7.005 | 0.62 | 0.021 | 0.036 |
| K2O | 0.408 | 7.005 | 0.62 | 0.021 | 0.036 | 11.77 |
| CaO | 0.009 | 0.009 | 0.007 | 0.007 |
| TiO2 | 0.021 | 0.036 | 11.77 | 0.008 |
| Cr | 0.036 | 11.77 | 0.008 |
| MnO | 0.008 |
| FeO | 0.008 |
| Ni | 0.008 |
| Cu | 0.012 | 0.009 | 0.009 | 0.007 | 0.007 |
| Zn | 0.009 | 0.009 | 0.007 | 0.007 |
| Sr | 0.009 | 0.009 | 0.007 | 0.007 |
| Zr | 0.007 | 0.007 |
| Mo | 0.007 |
| Traces: Rb Pd Ce Pb |

The samples looked by crapy, porous or rough fracture surface (Fig. 4). This rise the surfaces of the absorbents that facilitates water diffusion in to the absorbent. On the other hand, the decorated carbon micrographs of samples (Fig. 4) appear changes in morphology of phase for new irregular bulky particles presence on the surface. This leads to increased surface texture protuberance and coarseness that are absent before carbon loading [19-21].

Figure (4): FE-SEM images of carbon nanotube / (Bentonite) Clay /Fe$_2$O$_3$

E-DX is a versatile method utilized for qualitative and semi-quantitative analysis, it was noted that the iron in the (Bentonite) clay was increased in the presence of carbon and Fe$_2$O$_3$ impetration. For pristine (Bentonite) clay, it appear larger particle size and unequal particles due to stacking of flaky materials in comparison to the treatment with HCl and NaCl where these particles were disaggregated to smaller flakes and a clear microstructures several distinction (Figures 5).
Figure 5: E-DX analysis of carbon nanotube / (Bentonite) Clay / Fe2O3

Removal of Real Aqueous Pollutants by Using carbon nanotube Decorated on Clay (Bentonite) /Fe2O3

A real sample 100 mL of pharmaceutical pollutants with a refry concentration were using in this study, then added to a conical flask (Erlenmeyer) in the presence of 0.1g from prepared (C decorated (CNT) Clay (Bentonite) /Fe2O3 Micro/Nanocomposite), after that the mixture were putting in a sonicated water bath for 1 hr., after that the supernatant were separated via centrifuge and measured the remaining concentration via utilizing UV-Visible spectrophotometer at the $\lambda_{\text{max}}$ 279 and 272 nm for each drugs AMX and PHE at the same order [22-25] the result show in Figure (6).

Figure (6): Removal real aqueous pollutants by using Carbon NT decorated on Bentonite Clay / Fe2O3 Spectrum of drug (Exp. Condition: Temp. = 25°C, contact time 1 h, and pH = 6)

A Comparative adsorption between different source of carbon to removal Pharmaceuticals pollutant
A Comparative study between (commercial Sugar (Sucrose) / Clay(Bentonite) / Fe$_2$O$_3$ Micro / Nanocomposite, CNT / Bentonite / Fe$_2$O$_3$ Micro / Nanocomposite, AC / Bentonite / Fe$_2$O$_3$ Micro / Nanocomposite, CNT, AC and Clay(Bentonite)) as Adsorbents were carried out. The top data of removal (E%) for drugs (PHE and AMX) the order increasing: CNT / Bentonite Fe$_2$O$_3$ Micro / Nanocomposite > CNT > commercial Sugar / Bentonite Fe$_2$O$_3$ Micro / Nanocomposite > AC / Bentonite Fe$_2$O$_3$ Micro / Nanocomposite > Bentonite > AC [26, 27]. shows in Figure (7).

Figure (7): Comparative between commercial Sugar / Bentonite /Fe$_2$O$_3$ Micro/ Nanocomposite, CNT/ Bentonite /Fe$_2$O$_3$ Micro/ Nanocomposite, AC/Clay (Bentonite) /Fe$_2$O$_3$ Micro / Nanocomposite, CNT, AC and Bentonite clay

A comparative adsorption between sonication and water bath Shaker to removal Pharmaceuticals pollutant

A comparative between sonication and water bath Shaker by using CNT/Clay (Bentonite) /Fe$_2$O$_3$ Nanocomposite show in figure (8). The best data of the removal percentage (E%) of sonication 90.9%, 81.812% and Shaker 60.11%, 50.2% for drugs (Phenylphthrine PHE and Amoxicillin AMX) respectively [23, 28, 29].

Figure (8): Comparative between Sonication and Shaker by use CNT/ Bentonite /Fe$_2$O$_3$ Micro/Nanocomposite
4. Conclusion

1- Good removal of Pharmaceuticals pollutant from aqueous solution by using CNT/clay (Bentonite) / Fe$_2$O$_3$ Micro / Nano-composite.

2- The best data of the removal percentage (E%) of sonication comparative with Shaker for PHE and AMX drugs.

3- Removal of real Aqueous Pollutants by Using Carbon NT Decorated on Clay (Bentonite) / Fe$_2$O$_3$ after 1h gave very high the percentage of removal (E%) and very low absorbance about (0.0001).

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