A new adsorption material based GO/PVP/AAc composite hydrogel characterization, study kinetic and thermodynamic to removal Atenolol drug from wastewater

Asawer A. Mhammed Alzayd, College of Veterinary Medicine, University of Kerbala / Iraq
Ahmed Issa Atyaa/ Thi-Qar General Directorate of Education, Ministry of Education, Thi-Qar/Iraq
Nadher D Radhy / College of Education/ University of Al-Qadisiyah/ Iraq
Layth S. Jasim Al-Hayder / College of Education/ University of Al-Qadisiyah/ Iraq
Corresponding Author E-mail: a.asawer@uokerbala.edu.iq

Abstract
Increased contamination of pharmaceutical compounds and their presence have led to real health problems. In this study used Poly (Graphene oxide /polyvinylpyrrolidone /acrylic acid (GO/PVP/AAc) as the innovator composite/ hydrogel, were tried out atenolol drug. It has been proven to be effective in laboratory elimination of solutions. The composite preparation via free radical polymerization by using Specific ratios between (PVP/AAc) hydrogel and graphene Oxide (GO). The innovator adsorbent was estimated characterized by FT.IR, and FE-SEM. A suite adsorption tests were studied using to performed the Optimal conditions Of which contact time, pH. Dosage of adsorbent, ionic strength, and temperature. The kinetic experimental data were carried out via two model first pseudo order and second pseudo order, the adsorption process followed Pseudo second -order kinetic model with correlation coefficients greater than 0.999. The adsorption isotherms of composite could be illustrated well by the Freundlich Langmuir and Timken equations, The process of Atenolol adsorption on composite was depended on Freundlich and Timken isotherms more than other. The study discusses the thermodynamic parameters including changes in enthalpy , , entropy, and Gibbs free energy.

Keywords: Atenolol, hydrogel, Cross-linking, GO, Adsorption, biological half-life, pollution.

Graphene

1. Introduction
It is has become the Planet Earth full of contaminations which resulted from human activities whether related to industry or many process concerning chemical experiments ,wars, pesticides, health operation ,drugs and misuse of consumable so pollutants can be classified to: I-radioactive - II-biochemical material- III-organic pollutants- IV-inorganic pollutants [1,2]. In recent decades observed spread of cancer diseases increase frighteningly of the main causes of speared of this disease is pollution ,because the pollutants produced free radicals in organism body when transport by water ,food and air ,hence the
interest of researchers is focused on reducing pollution in all forms and ways like ion exchange, chromatography, photo catalytic, member filtration and ultrasound[3,4]. There are more than 4000 active medical compounds used in different countries of world (human and veterinary) used intensively[5]. Researchers found highly concentration from in sewage and hospital water pharmaceutical industries, atenolol is one of beta bloker drugs used to treatment hypertension and other cardiovascular disease (CVD) [6]. the studies have proven this drug is low absorption in colon and intestine so have short half-life[7]. the human body was eliminate with urine stool or sweat. the formerly studies confirm this drug can be remains 166 day. the other side effect to this group of type drugs accumulated on central nerves system (CNS) in human and animals also caused the endocrine-disrupting effects so we need to thought how we can increase biological half-life to increase effectiveness activity to drugs addition Reduce pollution this composite may be Benefit as drug carrier[8,9].

The adsorption technology is the easiest, cheapest, simplest and most effective in removing pollutants[10]. the carbon compounds and polymers known used in many fields e.g. purification Graphene oxide (GO) is a two-dimensional (2D) nanomaterial with a large planar size and an atomic thickness. Moreover, GO possesses large specific surface area[11,12], hydrogel is one of kind hydrophilic polymer three-dimensional crosslinking network and have many groups loving water like hydroxyl sulfonyl, amine, amide and carboxylic acid so hydrogel have high bulge capacity[13]. In this work prepared successfully (GO/PVP/AAC) composite. also will focused effectiveness of was the composite graphene oxide/polyvinlypyrrolidoe/acrylic acid (GO/PVP/AAC) which was recently applied to adsorption of some dyes and we will try it to removal beta blocker drugs also this work showed effect some change parameter like PH, time, ionic strength and temperature its most importance to develop effective materials for the removal drug active compound from the aquatic environment.

2-1. Instruments

UV-Visible Spectrophotometer, Single Beam, UV -7310, Jenway, UK, UV-Visible spectrophotometer, Double Beam, Shimadzu. PC 1800, Japan. Hotplate-Stirrer, L-81, Jlabtech, Korea, Electronic Balance, Sartorius Lab. L420 B, +0.0001, pH-meter, pH-3110, Intertek, Germany, vacuum oven, K-VO27, K&K, Korea Dunboff metabolic shaking Incubater GCA/ precision Scientific, 54160, Hitachi, Japan, Sonication path, LUC-410, Labtech, Korea, Centrifuge tubes D-78532 Tuttlingen
6000 U/min. Germany whole the reagents used were analytical class, pure with no further purification, and all the solutions were prepared with deionized water

2-1. Chemicals & reagents

Acrylic acid (AAc), and polyvinylpyrrolidone (PVP) were supplied by (Himedia, India). N,N’-Methylene- bis-acrylamide (MBA) as cross linker, was purchase from (Sigma-Aldrich, Germany). The initiator is potassium persulfate (KPS) was supplied by (merck, Germany), Ethanol, Sodium nitrate, and Potassium permanganate, Hydrogen peroxide (30%) were supplied by (Fluka, Germany). Atenolol {ATL} was purchase from (Basic Pharma Life Science Pvt.Ltd, India) Sulfuric acid, and Graphite (5 μ m), supplied from (BDH, Chemicals, England). Sodium chloride, Potassium chloride, Carbonate Calcium, Sodium Hydroxide and Hydrochloric acid were provide from (Fluka, Germany).

2-2. Preparation of (GO/PVP/AAc) composite

The GO / PVP – AAc composite prepared was carried out in several stages:

Stage1: Preparation of graphene oxide

Hummer Method was using to prepared GO by outfit an icebath at Cº and adding 46ml from sulfuric acid to conical flask Followed by adding 1gm from Both of graphite powder and sodium nitrate, The mixture was magnetically stirred for 3 h ,thereafter added 6 gm from KMnO₄ gradually with 100ml D.W and continuous stirring for 2h in room temperature, then transferred to hot water bath with adding distill water until converted solution color from green to brown , Add 60 mL of hydrogen peroxide (30%) turned to the bright yellow that indicate to formation GO later washed and dried [14,15].

Stage2: Preparation of GO (PVP/AAc) composite: included three major steps

step1: prepared a group of solutions (1.0-0.2)w/v% from GO dissolving in distill water by usage ultrasonic bath apparatus.

step2: prepared (PVP/AAc) hydrogel by mixing 20% PVP and 80%AAC respectively followed by many process of additions like KPS as Initiator (generate free radical) and MBA as crosslinked, then passed on nitrogen gas to remove
dissolved oxygen then leaved mixture in water bath for 2 h to complete the polymerization process, later washing and drying [16].

step 3: repetition preparation (PVP/AAC) hydrogel from blended component polymer (20,80) % respectively and mixing with the solutions prepared in the first step by added 1 ml from GO solution and 10 ml from solution component hydrogel and repeated similar processes in step 2

2.3. Characterization composite:

The structure of composite with Fourier transform infrared spectroscopy (FT-IR) recorded on with a (Shimadzu, Japan, 8500) FT-IR spectrometer, employ the KBr within a range of use (400 – 4000) cm⁻¹. Morphological studies were observed by field emission scanning electron (FE.SEM) analysis. Its accomplished through, using (JEOL, JSM-6701F, Japan) microscope with an acceleration voltage Informs 8.0 kv

2.4. Adsorption Experiments

Adsorption of atenolol from aqueous solution onto GO (PVP/AAc) composite conducted by the batch adsorption system. All of experiments were achieved in stoppered Erlenmeyer flasks, fixed weight of composite 0.05 g. In all experiments, fixed volume (10 ml) from different concentration solutions aqueous drug (10-100) mg/ml the mixture in stoppered flask was shaken in a shaker incubator a thermostatically at speed of 150 rpm until reached equilibrium in 90 min, the equilibrium time was fixed in all adsorption experiments the suspensions put a centrifuged at 6000 cycle/ min for 10 min, then estimate amounts of adsorbate by measure in U.V visible spectrophotometer at λmax (275.5) nm, A batch of experiments to investigated different parameters as weight of adsorbent contact time pH, temperature and ionic strength calculate amount of drug adsorbed by the following equation

\[ qe = (C_0 - C_e) V / M \]

Where \( qe \) is the quantity of absorbate (mg/g), \( V \) is the volume of solution of the absorbed Material (L), \( C_e \) is the equilibrium concentration (mg/L), \( M \) is the weight of absorbed (g), and \( C_0 \) is the initial concentration (mg/L) [17]

3. Results and discussion

3.1 Characterization of GO, P (PVP-AAc) and GO/P (PVP-AAc)
3.1.1 FTIR analysis:

The various functional groups to the (PVP-AAc)hydrogel , GO/P (PVP-AAc) composite and composite loaded with drug, were measured by FTIR spectroscopy, as shown in Fig (1). Comparing the spectra of PVP/AAC hydrogel the following was observed, Wide absorption band between the range (3500-2600) cm\(^{-1}\) in spectrum hydrogel, which indicate interfering between the O-H , N-H , methylene aliphatic vibrations symmetric , asymmetric and aromatic stretching vibrations. The carbonyl group of amide followed to crosslinked(MBA) seen in1650 , while the stretching vibrations carbonyl group C=O, of carboxylic acid seen in 1736 , additional stretching vibrations around at range (2460-1000)cm\(^{-1}\) were related to O-H, N-H bending and ,C-C ,C-N,C-O bending . In case of composite spectra noted the shifted to some functional groups absorption peaks especially in carbonyl area. Stretching vibrations to carboxyl and amide groups were shifted to low vibrations because formation hydrogen bonds[18,19]. The FTIR spectrum to composite loaded with drug appeared more nip up and spectrum shows an increase in the bands. In more than one area to denote occurred adsorption drug on surface composite, the absorption peaks showed new bands in highly wave number (3550-2600)cm\(^{-1}\) which attribute to primary and secondary amine Attributable to drug, also Stretching vibrations (C-H) to methyl and aromatic groups, abroad peaks at (2560-2530)cm-1 belong to a neoteric interactions between functional groups to drug and composite lead to appeared overlapping, the vibration of carbonyl groups reduced to lower wavenumber due to hydrogen bonding .Additional a new stretching vibrations shown at (1300-1100)cm-1 refer to (C=C) aromatic. All of shifited peaks detected to occurred adsorption drug on composite[20,21].
Fig(1)FTIR spectrum of atenolol loaded on composite, P (PVP-AAc) and GO/P (PVP-AAc)

3.1.2 Morphological studies:

To observed the morphology characterization of the composite, used field emission scanning electron the pictures taken in different magnification forces before and after adsorption .Fig (2) a,b shown composite in 2 µm and 500nm Respectively in the first magnification forces the composite surface shape appeared gruff, Wavy irregular , in second magnification forces seen composite like a porous network like spongy layers . The images in fig (2) a,b, it was shown surface after adsorption drug, its appeared like a small ball-shaped agglomerates , the porous network supply many adsorption position[22]
3.2. Adsorption results:

3.2.1. The influence of weight adsorbent: It was observed adsorption of drug from solution when usage of different range from weight of composite (0.01-0.30) with 50 mg/L from atenolol drug increased with increasing surface weight
until reached to 0.1 gm , that was indicated to fill all active site in surface composite ,also due to occurred saturation state and equilibrium also increase the electrostatic attraction forces between adsorbate and adsorbent, fig (3) Shown effect dosage of adsorbent.

Fig(3) Effect of different adsorbent dose on adsorption at 25°C, 90 min, pH =6

3.2.2. **The influence of Adsorption time:** One of significant agent impact on capacity adsorption The removal of drug was study in concentration of (50 mg / L) at 25°C, a pH of 6 is examined at different time intervals, figure( 4), as shown the adsorption of drug on the surface of the composite, as noted the adsorption of drug increase with an increase of time until reached 90 min. After that time it stopped, because all active site of composite is reached to saturated state because it loaded with adsorbate[23].
3.2.3. **The influence of pH value:**

One of significant agent impact on adsorption capacity, The effect of pH on atenolol adsorption was estimated at (Atenolol concentration (50 mg / L), temperature, 25°C 150 rpm, adsorbent mass adsorbent 0.1 gm and contact time 90 min). It was noted that the amount of adsorbent increases with the increase of acidic function, until reaching the pH=6 which represented the optimal acid function, used pH at range (1-10) fig(5) demonstrates quantity of adsorption increases at range(1-6) then began decrease with continuous increase acidic function ,to interpreting that Initially you should exhibited the kinds of active groups in both the drug and the composite fig(6) assistance to elucidation .the composite have many functional groups as epoxy(C-O-C) ,hydroxyl (-OH) ,carboxyl (-COOH) ,carbonyl (C=O) ,chromene and many oxygenated functional groups[24,25],this groups has been hydrophilic behavior and effected with change pH It can be exposed to protonation and deprotonation[26] ,To become ionizable and carrier negative , positive or neutral charge . furthermore the atenolol drug have amide ,secondary amine ,carbonyl and hydroxyl groups[27].

![Fig(5) effect of pH on (atenolol) drug at 25°C,90 min](image)

the atenolol drug have pKa 9.4 in acidic media became carried positive charge focus on amide and amine groups[28] .Its a same charge on the adsorbent ,so there will be electrostatic repulsion between similar charge, thus for that reason the adsorption capacity is reduced at range (1-4) acidic function, But also note that these media are not free of adsorption , this is due to electrostatic attraction between
the negatively charged groups (-COO\(^-\)) Affiliate to surface composite and the positively ones of adsorbate(-NH\(^3+\)) to occurred partially adsorption as the following equations:

\[
\text{Composite}^{\text{COO}^-} + D^{\text{NH}_3^+} \xrightarrow{\text{(1-4)pH}} \text{Composite}^{\text{COO}^-} \text{NH}_3^+D
\]

At range (6-7) pH under these conditions the number of carboxyl group still carried negative charges on the absorbent surface, whereas the positively charged stay Conservative and another converted to (-NH\(_2\)) on the adsorbate surface, so removal drug from solutions via H-bonding and electrostatic attraction,

\[
\text{Composite}^{\text{COO}^-} + D^{\text{NH}_3^+} \xrightarrow{\text{(6-7)pH}} \text{Composite}^{\text{COO}^-} \text{NH}_3D
\]

In the basic media the adsorbate-adsorbent interaction hydrogen-bonding only so decrease capacity of adsorbate. Addition other Different forces Contribute to the adsorption process like vander waals forces, pi-pi interactions between aromatic ring in drug atenolol and the localized pi electrons aromatic ring in composite and London forces\([29,30,31,32]\).the results was similar in research previously from Nathalia K. Haroand and others to removal atenolol drug from activated carbon from best acidic function is 6 and contact time\([33]\).
Fig(6) clarifying functional group on composite GO (graphen oxide), ALT (atenolol drug), D (drug).

2. 2.3. The influence of ionic strength: The Hospital sewage containing drugs has ordinarily higher different types of salts, salinity of solutions effect on adsorption process in varied media was investigated, the results are illustrated in Fig(7), It turns out the capacity of adsorbate decrease dramatically with increase amount of types added salts (NaCl, KCl, CaCO3) at different concentrations ranging from (0.005-0.250) gm. to explain it, used some Theoretical proof, when bonding forces between the adsorbent surface and adsorbate ions electrostatic attractive, as in our system, an rising in ionic strength will decrease the adsorption intensity. on the contrary, when the bonding forces electrostatic repulsion, an increase in Ionic force will increase adsorption process[36]. In first case that mean added positive ions will done compete on active site with adsorbate, the salt ions penetrated into the composite/hydrogel network and combined with ionized groups of composite network, leading to the shielding effect and weakening the electrostatic attraction, also noted the influence divalent that effects on quantity adsorbate that appears more powerful from monovalent, electrostatic attraction between calcium ion have divalent it was stronger than monovalent K+, Na+ because operating a complex with surface composite to worked on reinforcement entanglement one molecule from Ca^{2+} could squat two sites from composite so decrease in amount of adsorbate. This is called the charge
effect, The effect of radius that was evident with Ionic remained Na⁺,K⁺, the molecule have small radius effected lower on adsorption. Also increase monovalent K⁺,Na⁺ can cause the contraction of adsorbent[37] pores, resulting in that some adsorbate could not enter into pores Conclude from above the resource Electrostatic attraction An important element of each adsorption process because it has highly sensitive with changing electrolyte and concentration of electrolyte each adsorption process Wang et al They mentioned and confirmed this fact in their report(2009) [38-39]. Indirectly ionic forces effect on Gibbs energy ΔG when ionic strength was increased, the electrical double layer bselement of adsorbent surface was compressed this behavior lead to a decrease in electrostatic potential, so ΔG contributes to the total free energy change of adsorption process[40].

Fig( 7) Effect of ionic strength on adsorption of drug at 25°C,90 min , pH =6

3. 2.5. The influence of temperature: The temperature play vital role in the adsorption process, the effects of temperature was carried out at different temperature (15-35°C),The fig(8) shown the amount of adsorbate decrease with increase temperature, also that is point out the adsorption process was exothermic and that belong the to the molecules adsorption acquisition kinetic energy with increase heat so separate from superficies adsorbent, addition raised temperature will increase the solubility of the adsorbate Consequently, affinity decreases towards to surface adsorbent. Also raised the temperature may be due to breaking some active functional group lie in a rim surface composite so decrease in number active site [41,42]
4. Adsorption Isotherm and thermodynamics: adsorption isotherms are of fundamental significance to better investigate the adsorption mechanisms, design of adsorption systems one of the most useful data to understand the mechanism of the adsorption. The results show that The adsorption isotherm corresponds with S4 according to Giles et al. (1960) [43], its assumed that the molecules drug towards perpendicularly on surface adsorbent the fig(9) shown it. Three isotherm models called, Langmuir, Freundlich and Timken, analyzed the empirical data. Langmuir model can be used to explain homogeneous of adsorption process, Freundlich model assumed the adsorption was heterogeneous of adsorption process, Timken to calculate heat of reaction, the study Applicable with freundlich and Timken isotherms that indicate the adsorption multilayer because the surface of composie have heterogeneous energy in active site, enthalpy value can be estimated by Vant -Hoff equation and plotted In Xm Varus1/T can extracted reaction of enthalpy slop = (-ΔH/R). Table (1),Table (2) shawed The correlation coefficients and constants of isotherm of Langmuir, Friendlies and Timken of Thermodynamic parameters Gibbs free energy (ΔG) and entropy change (ΔS)of adsorption process were calculated via impulse equilibrium results. the results showed in Table (3), negative entropy value point to adsorption regulars system and free energy have negative to refer to spontaneously [45-46].
Fig 9. Adsorption isotherm of (ALT) drug at 25°C, 90 min, pH = 6

Table 1. Effect of temperature on highest adsorption of drug(atenolol) on Surface GO/ (PVP-AAC)

| Temp.(C) | Temp.(K) | 1000/T(K) | Ce= 43.9 |
|----------|----------|-----------|----------|
|          |          |           | Xm       | ln(Xm)  |
| 15       | 288      | 3.472222  | 86       | 4.454   |
| 20       | 293      | 3.412969  | 69       | 4.234   |
| 25       | 298      | 3.355705  | 56       | 4.025   |
| 35       | 308      | 3.246753  | 44       | 3.784   |

Table (2) The correlation coefficients and constants of isotherm of Langmuir, Freundlies and Timken of

| Lang | Frend | Temk |
|------|-------|------|
| K<sub>L</sub> | q<sub>m</sub> | R<sup>2</sup> | K<sub>F</sub> | n | R<sup>2</sup> | K<sub>T</sub> | b | R<sup>2</sup> |
| -0.0156 | -16.129 | 0.382 | 0.0107 | 0.447 | 0.900 | 0.060 | 60.12 | 0.980 |
Table (3) Values of thermodynamic functions of adsorption process of atenolol drug on the adsorbent surface at 25 °C

| ΔH       | ΔG       | ΔS   | Equilibrium Constant(K) |
|----------|----------|------|--------------------------|
| -24570.400 | -6307.950 | -61.283 | 12.756                   |

3-4-5. Adsorption kinetic

To describe speed of drawing drug particles on surface composite used two equation models pseudo-first order and pseudo and second order the table, plots are shown in Fig, also shows the values of kinetic parameters ,qe ,coefficient and R₂, plots displayed that the adsorption followed pseudo-second-order kinetic model [47] We can get it values k₁ from the slope when drawing linear plot between ln(qe - qt) versus t.to get qe and k₂ drawing the linear plot between t/qt versus t the results shown in table 4.

Table 4: Correlation coefficients and kinetic constants of adsorption atenolol drug on composite surface

| First Order | Second Order |
|-------------|--------------|
| k₁  | qₑ   | R²  | qₑ   | k₂  | h     | R²  |
| 0.028 | 2.557 | 0.776 | 9.615 | 0.0448 | 4.1493 | 0.999 |

Conclusion

In this study, used Hummer methods to synthesis composite GO/PVP/AAC then tried out adsorption atenolol drug from solution, It has proven effective highly efficiency for removing drug and has reached to 90.2%, the composite found out were characterized via FT-IR, and FE-SEM. FTIR spectra of the composite before and after the adsorption were accomplished, in order to demonstrate the nature of the functional groups. Used field emission scanning electron to detected the morphology characterization its appeared as porous network and seen as spongy irregular layers composite. Through the experimental data its could be fixation of optimum conditions, the best pH for atenolol adsorption was (6),suitable contact time of the process was 90 min, better dosage form of adsorbent 0.1gm , the results also noted negative effect to increase temperature and ionic strength. The isotherm model that best agreement with Freundlich, To indicating the adsorption process is multiplayer Also the adsorption isotherms applied with type S-type. The kinetic
experimental data for the studied systems best fitted to the pseudo-second order model, additional calculated the thermodynamic functions of the process of adsorption of obviously the process exothermic, spontaneously reaction and highly regular.

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