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Study of Sorption Kinetics of Doxycycline on pH Sensitive Hydrogel-based Graft Copolymers of Chitosan/Arabinogalactan/ Gummiarabic with Vinyl Monomers

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ABSTRACT

Graft copolymers of natural polysaccharides chitosan (*Chs*), gummi-arabic (*GA*) and arabinogalactan (*AG*) were synthesized with N-vinylpyrrolidone (*VPr*) (4-vinylpyridine and N-vinylpyrrolidone used as comonomers for chitosan grafting), and then pH-sensitive hydrogels were designing by cross-linked them with N,N-methylene-*bis*-acrylamide. Effective sorption of doxycycline from aqueous solutions with water-swelling gels has been studied experimentally. The effect of gel dose, initial concentration of doxycycline, pH medium and solution ionic strength of the sorption rate and capacity of the antibiotic was systematically studied. The surface and volume absorption kinetics and isotherms of the process have also been investigated. It was found that the max sorption capacity for swellable gels varies between *Chs-graft-VPr/4VP>AG/graft-VPr>GA/graft-VPr*. It has been shown that the sorption mechanism is mainly dominated by physical sorption and to some extent hydrogen bonds and electrostatic interactions.

Keywords: Chitosan, Gummiarabic, Arabivogalactan, Graft copolymer, Hydrogel, Doxycycline, Sorption.

INTRODUCTION

It is known that antibiotics are widely used in modern medicine in the treatment of inflammatory diseases, destruction or inhibition of bacterial cells[1,2]. Doxycycline *(Dox)* is one of the anthracycline series of antibiotics which is currently used in inflammatory diseases of the respiratory and gastrointestinal tract[3-5]. *Dox* is a broad-spectrum antibacterial drug consisting of free -OH, -NH_2 and carbonyl groups. Doxycycline is a semi-crystalline antibiotic and is used to treat superficial diseases of the eye, periodic epithelial erosion, and corneal wounds[6-8].

Sorption of antibiotics by ion exchange materials is widely used in their separation and purification processes. There is also some scientific research in the periodical literature on the sorption of antibiotics by polymer sorbents and the study of thermodynamics and kinetics of the process[9,10]. The inclusion of drugs in polysaccharide macromolecules not only reduces their adverse effects on the body,

but also increases their bioavailabilities.

In addition, some drugs pollute the environment after use, which has a detrimental effect on humans, animals and plants[11,12]. *Dox* is widely used in agriculture, causing more environmental pollution[13]. It is known that this antibiotic is not fully absorbed and 30-90% of the dose is excreted without biological activity[14]. Separation of *Dox* from polluting water to prevent such adverse effects is an actual topic. Research on its adsorption of *Dox* on organic, inorganic and hybrid polymeric materials can be found in the literature[15-20].

From this point of view, the effective removal of *Dox* with natural polymer-based hydrogels is an urgent problem. The synthesis of new types of hydrogel materials is of great interest. In the literature, sorption of *Dox* with *Chs, GA* and AG-based hydrogels is highly preferred. Because these polymers have great potential in the industry and we can briefly mention the following about them. *AG* is a hyperbranched natural polysaccharide which has gasprotector, membrane-conducting and high sorption capacity properties. It is widely used as a carrier of enzymes, drugs and essential minerals for the human body. The *AG* macromolecule has a highly branched structure (Fig. 2): the main chain consists of a galactose chain connected by a β-(1→3) glucoside bond. The side chain is composed of uronic acids, mainly glucuronic acids, which bind to the galactose and arabinose links by a β-(1→6) bond[21-24].

Chs is a polycationite type natural linear structural polyaminosaccharide obtained from chitin by deacetylation process. Chitosan is composed of randomly distributed of β-(1,4)-2-amino-2-deoxy-glucosamine and β-(1,4)-N-acetyl glucosamine units[25-27]. The high sorption capacity due to metal ions, non-toxicity, and drugs, and easily chemical functional of *Chs* macromolecules confirm that its perfect chemical and physical properties in delivery of biological active compounds in biotechnology and stabilization of antibacterial metal nanoparticles[28-31].

GA, a natural polysaccharide, is a biologically inert polymer used in medicine to make soft and hard capsules and to make high sorption adsorbents. The *GA* macromolecule has a hyber branch chemical structure (Fig. 2). Its elemental link consists of pentose, methyl pentose, hexose and polyuronic acid units combined with each other[32,33]. The main skeleton of the *GA* macromolecule is composed of galactose and mannose, and the side branches are composed of pentose and xylose units. In the present study, pH-sensitive gels were synthesized from the cross-linking of *Chs VPr* and *4VP* graft copolymer with glutaraldehyde, and *GA* and *AG VPr* graft copolymer cross-linked with *MBAA*. The structural characteristics of the gels were studied and the sorption isotherms of doxycycline were investigated. The parameters of antibiotic separation from the aqueous solution were also determined and the sorption results were applied in different kinetic models.

EXPERIMENTAL

ChS (deacetylation degree and average molecular weight are 87-90% and 35 kDa, respectively), *AG* and *GA* were obtained from Sigma Aldrich (*AG*, 200 kDa; *GA* 400 kDa). Glacial acetate acid, acetone (≥99.8%), ethanol (95%), diethyl ether (≥99.6%) and MBAA also from Sigma-Aldrich co ltd. As initiator used 2,2-azobisisobutyronitrile (*AIBN*) and *4VP* (assay 95-96%), *VPr* (≥99%) were also purchased from Acros Organics and had been distilled and recrystallization before the use. All solvents were purified by distillation, according to the conventional methods and were purchased from Sigma Aldrich. *Dox* with the empiric chemical formula $C_{22}H_{24}N_2O_8 \times HCl \times 0.5H_2O \times 0.5C_2H_6O$ was obtained from Merck.

Gel preparation

ChS (AG or GA) is dried at 40-50°C (24 h) suspended by 150 mL of 2% CH_3COOH, then 1-2 hmixing. 2 mL monomer`s - *VPr* and *4VP* (1:1 mol ratio) were added to the *Chs* solution and continuously stirred in 30 min (*VPr* only for *AG* and *GA*). The reaction was performed according to the method[21]. Graft-natural polysaccharides (graft-Np) copolymer samples are mixed with a cross-linking reagent and gelation obtained within 30 min (65-75°C). Prepared all three natural based hydrogels were washed with bidistilled water and ethanol, respectively[21].

Characterizations

The infrared properties of the *Chs, AG* and *GA* graft copolymer based hydrogel and hydrogels-*Dox* simples were analysis by Fourier transforms infrared spectrophotometer (FTIR) in the 4000–400 cm^{-1} range by Nicolet 6700, (USA) instrument. Nanosized Zetasizer ZS90, Mulvern instrument used for measurements of surface zeta potential of obtained hydrogels. The initial and equilibrium concentrations of *Dox* in aqueous solution were determined by an ultraviolet spectrophotometer at 349 nm (UV-Vis 2550, Shimadzu, Japan).

Adsorption experiments

The doxycycline removal experiments for the three different hydrogel samples were conducted with a 90 mg/L initial concentration[16]. Ten mL of the antibiotics solution was mixed with natural based hydrogel (4 mg) at different pH, removal times, and temperatures. The samples were filtered with specific filters from Millipore prior. The calibration curves of various antibiotics concentrations were established from 10; 20; 40; 60 and 90 mg/L concentrations with best linearity in all circumstances.

Adsorption isotherms for the all hydrogel simples performed the following method. Ten mL solutions of the neutral pH antibiotics solution with different concentrations (10, 20, 40, 60 and 90 mg/L) were mixed and stirred at 20ºC temperature with the hydrogel graft-Np (4 mg) at different contact times for *Dox* antibiotic. Equilibrium condition determination experimentally, for the *Dox* adsorption according to the method[34]. Concentrations of antibiotics were determined as described above due to the method. Adsorption capacity of graft-Np, Qe, was calculated according to Eq.1:

$$Q_e = \frac{(C_0 - C_t)}{m} \times V \qquad (1)$$

Where, Q_e - is the equilibrium *Dox* sorption capacity (mg/gr), C_0 is initial and C_e is the equilibrium concentrations of antibiotics (mg/L), V=10 mL is the volume of *Dox* solutions, and m is of the graft-Np dose by mg.

RESULT AND DISCUSSION

In a previous study[21] author obtained the optimal graft co-polymer reaction condition of radical copolymerization of *VPr* and *4VP* into *ChS* macromolecule. For this graft co-polymers synthesis, *MBAA* as a specific cross-linker was prepared. The new pH sensitive hydrogels could form after chemical binding of graft-*ChS-PVPr-co-P4VP* simples with *MBAA* by radical reaction. This covalent binding occurred between -CH_2- groups of *PVPr*, -NH_2 groups of *ChS* and –CH< groups on *P4PV*. A possible radical chemical reaction mechanism of co-grafting could be shown in Fig. 1 by the author[21].

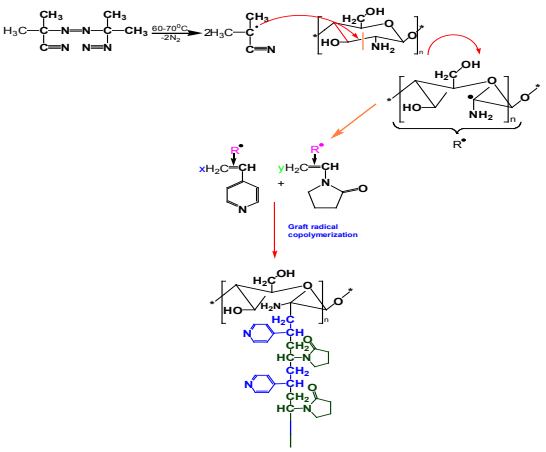

Fig. 1. The chemical co-graft radical polymerization reaction of *VPr* and *4VP* vinyl monomers with *Chs* chains

The FT-IR spectrum of *ChS* was characterized by intensive widespread peaks in 1656 and 1598 cm^{-1} of -NH_2 groups. The peak which is observed in 1260 cm^{-1} region belongs to C–N binding on *Chs*. The bands of characteristics for saccharide structure are at 1157 cm^{-1} (C–O–C), 1087 and 1032 cm^{-1} (C–O)[25]. The -NH_2 group has a shift from 1598 cm^{-1} to 1578 and 1578 cm^{-1} region in the spectra of the cross-linked CS based gel. Similar experiments were performed with *VPr* monomers of *AG* and *GA*, and copolymer samples with similar structure were synthesized. The cross-linking of these copolymer samples with *MBAA* resulted in the formation of hydrogels that can be swollen in water and pH medium. The synthesis and characterization of such hydrogels have been studied in detail in the work of Shamo *et al.,*[23,24]. In the structure, it is possible to imagine the chemical structure of the sample of graft copolymer obtained by replacing the *Chs* units with fragments *AG* and *GA*. *Dox* binding mainly occurred between –$OCOCH_3$, –COOH on *Dox* and -OH, -NH-groups of *ChS* the by hydrogen bond. Other chemical shifts involving C–O chemical stretching on Chs from 1755, 1087 and 1032 cm^{-1} to 1732, 1069 and 1024 cm^{-1} were due to that intermolecular hydrogen bond between *Dox* and *Chs*.

Addition, the FTIR spectra of *GA* and *AG* for the adsorption of *Dox* typical chemical peaks of polymer chains observed in different regions. In 3430 cm^{-1} peak concerning aromatic connected O–H, 1620 cm^{-1} of benzene ring C=C bonds, 1390 cm^{-1} to –COO–, and 1090 cm^{-1} intensive peak belongs to C–O–C bonds. After the adsorption of *Dox*, the peaks at 400–800 cm^{-1} interval belonged to the aromatic –CH chemical group of antibiotics, proposed that the antibiotic molecule was adsorbed onto the hydrogel surface layer. The peak shifted from 3430 cm^{-1} to 3440 cm^{-1} belongs to O-H, the peaks shifted from 1390 to 1430 cm^{-1} belongs of –COO– and the peaks shifted from 1090 cm^{-1} to 1100 cm^{-1} belongs to alkoxy C–O–C bonds after adsorption of *Dox* molecules. The double of C=C bonds peaks about to the aromatic group shifted from 1622 to 1631 cm^{-1} region after complexes of the *Dox*, show that the p-p electron-donor acceptor chemical force between Dox molecules and hydrogels was proposed as the important parameter for drug adsorption[40,41].

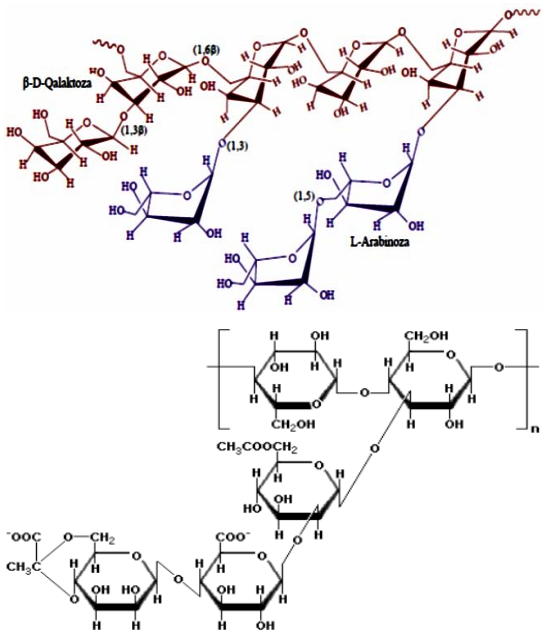

Fig. 2. Chemical structure of arabinogalactan (top) and gummiarabic (following)

The effect of the dose of hydrogels and the pH medium on the removal of the *Dox* antibiotic from the aqueous solution (Fig. 4). The degree of removal of *Dox* by *AG* and *GA* graft copolymer based gels is the same. Removal occurs at a higher degree in *Chs* graft with *VPr* and *4VP* copolymer based gels. This is due to the richness of the main macromolecule in terms of functional groups and the presence of *4VP* units in the *Chs* chain. The pyridine ring binds to Dox with $\pi \rightarrow \pi$ interaction. In *AG* and *GA*-based gel samples, the *Dox* interaction is mainly due to hydrogen bonding and electrostatic attraction[36].

The effect of pH of the medium and dose of gel simple on *Dox* removal was studied in detail (Figure 3).

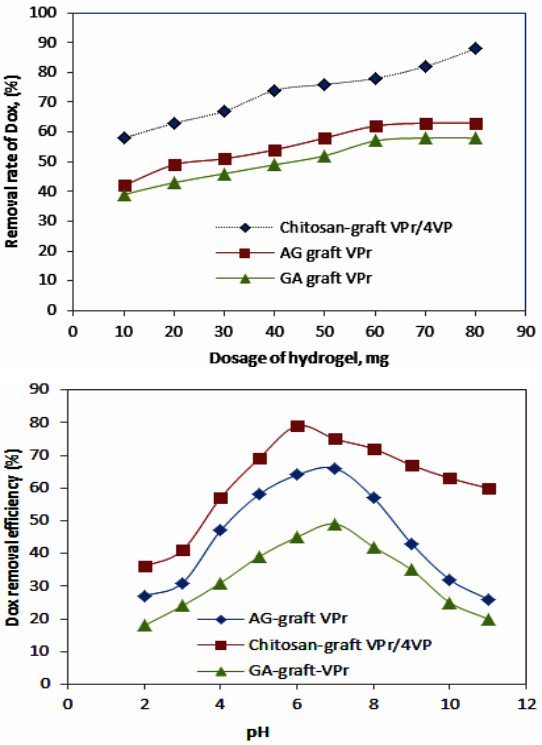

Fig. 3. The effect of the dose of hydrogel and the pH of the medium on the sorption of *Dox*. 20 mg/L was initial concentration of *Dox*, temperature 298 K and contact time was 24 hours

Shown that, the removal efficiency of *Dox* depends on from the solution pH, initially increased and then began decreased. Graft-Nps exhibited higher antibiotic capacity at neutral pH. According to the sorption result, the adsorption of *Dox* was highly pH-dependent, and the cross-linking chains of the hydrogels played an important role in antibiotic sorption. The medium of the pH affected the hydrogel top layer charge and also the *Dox* dispensation in solution. It is clear that, graft-Nps carried various O-containing –COOH and hydroxyl functional groups. Most of these chemical functional groups are positively charged due to the protonated acidic pH medium. The hydrogel surface`s chemical functional groups will become the deprotonation and negatively charged at higher pH.

It`s known that *Dox* has multiple –OH, -C_6H_4-OH, -NH_2 ionisable chemical functional groups hence can exist as an cation, anion and a zwitterion. This also makes it possess multiple values for pKa (acid dissociation constant). Between intermediate pH values it exists as a zwitterion[34,35]. When the pKa1=3.02 at pH<3.02 *Dox* exists as a Dox^+. When pK_{a2}=7.97 at 3.02<pH<7.97 medium antibiotic exists as a Dox^0. Between pH 7.97 and 9.15 it exists as *Dox* – and pK_{a3}=9.15 and also pH>9.15 due to the –C_6H_4-CO-O- moiety and tri-C=O system loss of protons antibiotic as an Dox^{2-}. The three different ionisable forms of *Dox* functional groups are shown in Figure 4.

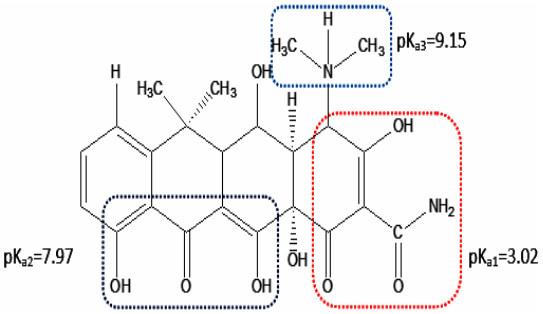

Fig. 4. The positions of different ionisable chemical functional groups of *Dox* chemical structure at different pK_a

The main form of *Dox* molecules would be zwitter-ionic and cationic types at pH≤7, and this form is effectively available for p→p electro-donor acceptor chemical interaction. This interaction formed with the pyridine ring structures of the *Chs* based hydrogel. When the pH values increase, *Dox* molecules begin to deprotonation and results decrease the π-withdrawing ability of the group. In addition, the electrostatic repulsion between the anionic form of *Dox* molecules and the functional groups deprotonated of natural based hydrogels increased with increasing pH values. At the end this leads to a decrease in sorption capacity.

The effect of Na^+ and Cl^- ions and non-electrolyte concentration on the sorption of *Dox* by hydrogel samples is shown in Figurs 5.

As can be seen, the antibiotic capacity of the *AG* and *GA*-based gel sorbents decreases as the concentration of NaCl in the solution increases. In *Chs* based gel, the antibiotic capacity increases to a concentration of 4 mg/L and then begins to decrease. However, the effect of electrolyte concentration on *Dox* sorption by *Chs* based gel is not so sharp. It seems that the interaction between the antibiotic molecule and the gel is stronger, and the concentration of Na^+ and Cl^- ions up to 10 mg/L has little effect on the weakening of these interactions. Such a strong interaction is due to the presence of a pyridine ring in the structure. Which proves the existence of the interaction π→π in this system. In *AG* and *GA*-based gel samples, the antibiotic capacity of the gel begins to decrease by more than 20% as the electrolyte concentration increases. Because in this case, the chemical bond does not occur, as in *Chs*.

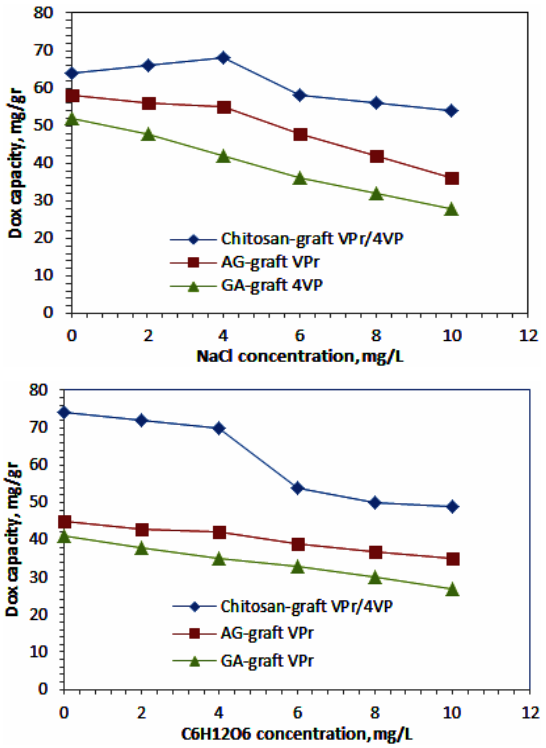

Fig. 5. The effects of NaCl and glucose concentration of *Dox* sorption by *Chs-graft-VPr/4VP*, *AG-graft-VPr* and *GA-graft-VPr* based hydrogel sorbents. C_{Dox} = 40 mg/L; hydrogel dose = 40 mg; T = 298 K; contact time = 24 hours

It is known that adsorption isotherms characterize the distribution of adsorbate molecules in different equilibrium concentrations in the liquid phase on the surface of a solid substrate. Thus, by applying the adsorption results to different isothermal models, it is possible to determine the nature of the interaction between the adsorbate molecule and the hydrogel. In this case, the perfect adsorption models are the Freundlich and Langmuir models (Fig. 6), and the linear dependence forms of these models are expressed by equations (1) and (2) below.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (2)$$

$$L_n Q_e = L_n K_F + \frac{1}{n} L_n C_e \quad (3)$$

Where C_e- is the concentration of *Dox* in equilibrium condition, mg/L, Q_e- is the amount of *Dox* adsorbed per gram of natural based hydrogel *graft-Np* at equilibrium condition, *mg/gr,* Q_m is the maximum adsorption capacity which is calculated by theoretical by *graft-Np* for *Dox*, *mg/gr,* K_L is a constant of Langmuir isotherm, l/mg, K_F is the empirical constant for Freundlich adsorption isotherm of the *graft-Np*, and 1/n is a the Freundlich adsorption constant.

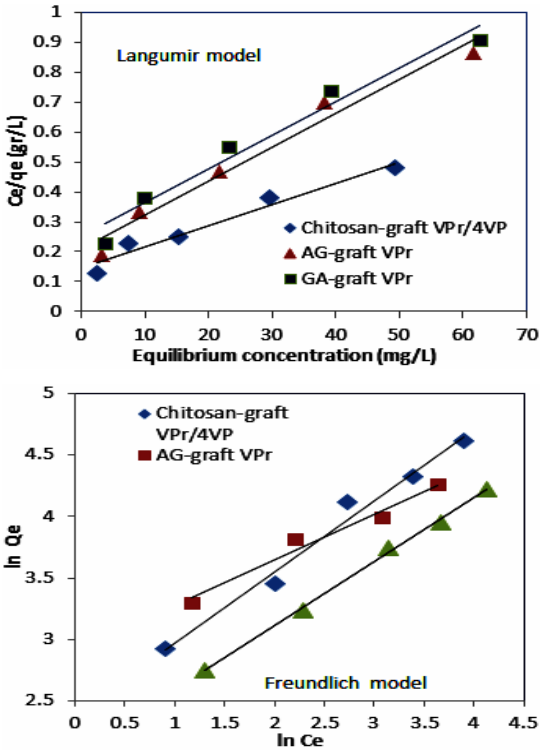

Fig. 6. Langmuir and Freundlich adsorption isotherms for *Dox* sorption by natural polysaccharide based hydrogel sorbent

The adsorption data of the studied *Dox* molecules onto *graft-Nps* were fitted with the Langmuir and Freundlich isotherms (Fig. 6). These two models, which can provide information on the 2 important parameters: adsorption capacity and affinity. The adsorption of *Dox* happened in a homogeneous surface of the natural based hydrogels according to the Langmuir model. But according to the Freundlich model the adsorption is not reversible, occurring by formation of multilayers of *graft-Nps* on a hydrogel surface[36,37]. The Freundlich model the best fitted for the adsorption process by *Chs* and *AG-graft* polymers based gel according to the R^2 correlation coefficient (Table 1). But *Dox* sorption data is best fitted with the Langmuir and Freundlich models for the *GA* based graft copolymer gel.

Table 1: Parameters of Freundlich and Langmuir isotherm models of *Dox* sorption with natural polysaccharide based gels

Hydrogel simples	Model	K_L or K_F	Q_m (mg/gr) or 1/n	R^2
Chitosan-graft VPr/4VP	Langumir	17.54	19	0.960
	Freundlich	1.06	0.052	0.982
AG-graft VPr	Langumir	5.05	18	0.965
	Freundlich	1.01	0.048	0.998
GA-graft VPr	Langumir	3.27	17	0.968
	Freundlich	0.98	0.059	0.971

The 1/n values of the constant were less than 1 due to the Freundlich model, and this indicated suitable adsorption process (Table 1). The Q_m- highest adsorption capacity for the *Chs* based graft copolymer, which was found to follow the physical-sorption mechanism adsorption of *Dox*. According to $R_L = 1/(1 + K_L C_0)$ equation Langmuir constant K_L can be calculated and presented in Table 1. The dimensionless separation factors calculated for *Chs* graft copolymer based gel is 0.006. The values of R_L for *AG* and *GA* based copolymer gels are 0.019 and 0.029, respectively. If the R_L datas were greater than zero and less than 1, these results showed favorable adsorption.

Forming stable adsorption and an effective system requires full understanding of the dynamic process of the sorption reaction. By using two kinetic models-pseudo-first order-PFO(4) and pseudo-second order-PSO (5) linear forms were applied of the studied of the adsorption kinetics of *Dox* systems (Figure 7):

$$\text{Ln}\,(Q_e - Q_t) = \text{Ln}\,Q_e - K_1 t \quad (4)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (5)$$

Where, Q_e is the adsorption capacity of antibiotics at the equilibrium state and Q_t is adsorption capacity of antibiotics at time of *t*; the *PFO* and *PSO* adsorption modulus are K_1 (1/min) and K_2 (g/mg×min), respectively.

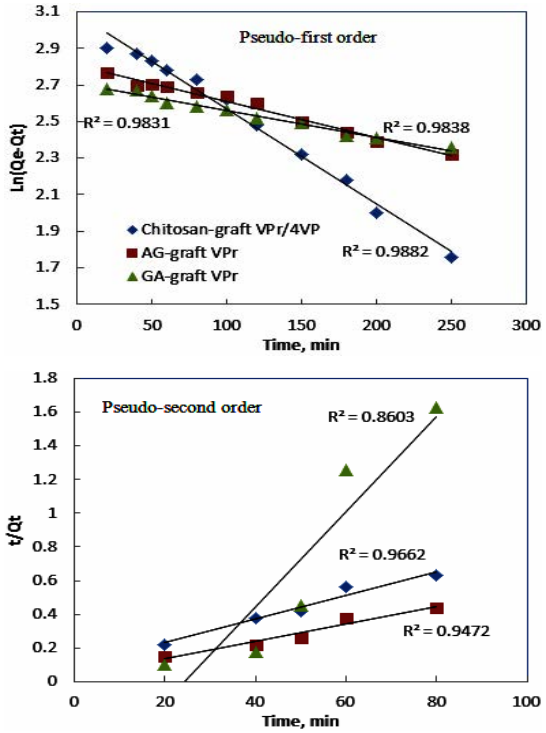

Fig. 7. Adsorption-*PFO* and *PSO* kinetic models data of the sorption of the *Dox* on natural based polysacharides

The R^2 correlation coefficient was 0.966 of the *PSO* model for *Chs* based hydrogels, and this data indicates the adequacy of this fitting model. The meaning of this finding is that the adsorption of *Dox* by *Chs* based hydrogel is assumed to be kinetically controlled as a *SO* reaction and the adsorption is dependent on the dose of natural based hydrogel and concentrations of *Dox* molecules. According to the *PSO* rate constant data the chemical adsorption mechanism involves electrostatic mutual attraction for *AG* and *GA* graft copolymer based hydrogel[37].

Thermodynamic parameter is necessary to determine the spontaneity or otherwise of an adsorption process. ΔG°-Gibbs free energy, ΔH°-enthalpy, ΔS°-entropy change, etc., are important useful thermodynamic parameters. These first three parameters are critically important for predicting adsorption mechanisms and thermodynamics, for the characterization and optimization of an adsorption process. The basic ΔG°, ΔH°, and ΔS° thermodynamic parameters were evaluated by (6)–(8) equations.

$$\Delta G = -RT\ LnK \quad (6)$$

$$LnK = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

$$K_d = \frac{Q_e}{C_e} \quad (9)$$

Where, K are Langmuir and Freundlich isotherm constant, L/mol; R = 8.314 J/mol×K is the universal gas constant. The plot of lnK values against 1/T, will give ΔH°, and ΔS° as the incline and intercept, respectively. The typical thermodynamic values for *Dox* adsorption onto different hydrogel are shown in Tables 2. Effect of temperature of adsorption process were conducted at 283, 2293, 303 and 313 K in 3 h and determined the following thermodynamic parameters.

Table 3: Thermodynamic parameter of *Dox* by natural based graft copolymer hydrogel

Polymer hydrogel	Temperature, (K)	K_d (Dimensionless)	Average ΔG° (KJ×mol^{-1})	ΔH° (KJ×mol^{-1})	ΔS° (J×mol^{-1})
Chs-graft VPr/4VP	283	1.47	-0.91	0.001	0.0032
	293	7.5	-4.99	0.067	0.0169
	303	3.05	-2.81	0.161	0.0098
	313	1.36	-0.79	-0.015	0.0025
AG-graft VPr	283	2.48	-2.14	-0.018	0.0075
	293	5.31	-4.14	0.035	0.0140
	303	9.34	-5.62	1.247	0.018
	313	3.49	-3.25	0.502	0.012
GA-graft VPr	283	2.19	-1.84	-0.024	0.006
	293	4.25	-3.58	-0.011	0.012
	303	7.20	-4.96	-0.114	0.016
	313	3.08	-2.91	-0.097	0.009

Table 2 showed that *Dox* adsorption onto different natural based hydrogels was predominantly an endothermic process. The endothermic nature of the sorption process suggests the possibility of multiple displacements of solvent molecules sequel to *Dox* adsorption onto the hydrogel surfaces and volume pores. Table 2 showed that the *Dox* adsorption was mostly physical (0<ΔH°<20 KJ/mol),

except for few studies that are predominated by physical-chemical adsorption. A positive ΔS°-value implies high hydrogel-*Dox* affinity during adsorption. Known that, pH medium changes the charges of hydrogel surfaces and drug molecules. From the Fig. 8 showed that at pH lower than the isoelectric point, hydrogels are positively charged. The pH higher from the isoelectric point gels in a negatively charged. The adsorption of *Dox* molecules occurs on the top layer phase of the hydrogel surface based on the surface potential data.

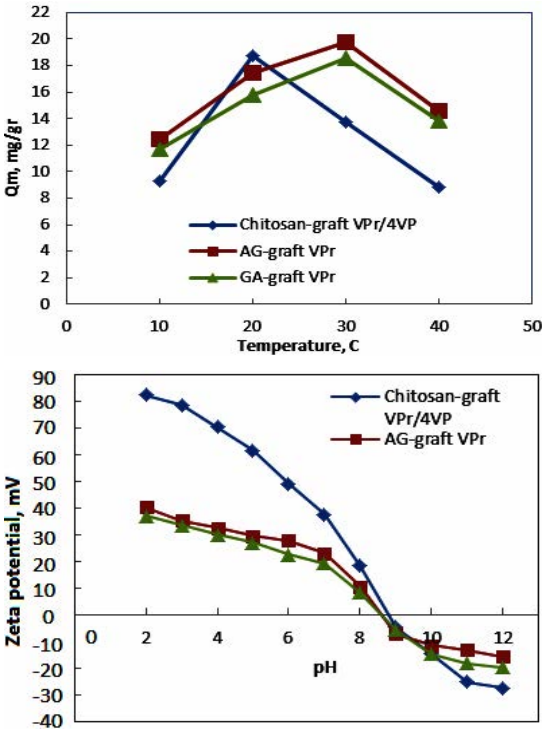

Fig. 8. Temperature depended on the adsorption of *Dox* by *Chs, AG* and *GA* based hydrogel and zeta potential of these hydrogels as a function of pH

The *Dox* antibiotic could chemical and physical interact more strongly with *Chs-graft* copolymer hydrogel surfaces with strong π→π electro-donor acceptor interaction. It showed that *Chs-graft* copolymer exhibited more sorption affinity for *Dox* molecules than by *AG* and *GA* based graft copolymer gels. *Ch-graft* copolymer structured more aromatic cycles and hydroxyl groups than *AG* and *GA*, which provide more π→π electro-donor acceptor interaction opportunities for *Dox*. Other hand, the hydrophilicity of *Chs-graft* copolymer based hydrogel was much less than that of *AG-graft VPr* and *GA-graft VPr* based hydrogels.

CONCLUSION

The specific chemical and physical sorption mechanism of doxycycline antibiotic adsorption onto *Chs, AG* and *GA* based hydrogels were thoroughly investigated. The isothermic values are well fitted by the Freundlich model for all experiments. Kinetic experiments showed that sorption data were best described by the pseudo-second order model. Adsorption process at different pH medium data`s confirmed that the sorption of antibiotic from medium by *Chs, AG* and *GA* based gels could be occurred by positive-negative charge interactions. This repulsion interaction occurred in the aromatic cycles and charged functional groups between the hydrogel and doxycycline. According to the data of the ΔG° energy the sorption process is spontaneous. Finally, the study showed that *Chs-garft-VPr-co-4VP* is capable of removal of doxycycline antibiotic from the aqueous solution (85-88%) at the optimized conditions and these matrices can be used as potential drug delivery in biotechnology.

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Conflicts of interest

The author declares that there is no conflict of interest in the present research work.

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