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Acceptance Letter

13 September 2017

Dear Dr. Layth Sameer Jasim / University of Al- Qadisiyah/Iraq

Mr. Wissam Litef penyan / University of Al- Qadisiyah/Iraq

Greetings

We would like to inform you that, your following paper was accepted and is selected for publication in: Vol. 9, No. 11-12, Upcoming Regular issues, 2017 of Journal of Global Pharma Technology/, (to get released on 17-21 December 2017).

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The adsorptive removal of Sulfadiazine drug from aqueous solution using poly (Acryl Amide-co-Crotonic Acid) hydrogels

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Abstract

The adsorption of Sulfadiazinedrug from aqueous solution has been investigated using acrylamide-co-crotonic acid croos-linked as the adsorbents. Batch kinetics and thermodynamics studies were carried out to evaluate the effect of contact time, ionic strength, pH and temperature. The calculated data were in accordance with Freundlich equation and the adsorption isotherms are of S-curve type according to Giles classification. The results obtained show greater adsorption uptake of the Sulfadiazine than Sulfathiazole on the hydrogels. The adsorption phenomenon was examined as a function of temperature (15, 25, 30 and 35^{o}C). The extents of adsorption of durg on the hydrogels were found to decrease with increasing temperature (exothermic process). The basic thermodynamic functions have also been calculated. Adsorption on hydrogels surfaces was examined as a function of pH. The adsorbed amount of drug on surface was increased as the pH decreased. The adsorption process is affected by the electrolyte concentration. The results indicated an increase adsorption of drug in the presence of sodium hydrochloride.

Keywords: Adsorption, Hydrogels, Sulfadiazine, Isotherms, Thermodynamic.

Introduction

Sulfadiazine (SDZ) belongs to the category of sulfonamides[1]. and considered as the first-generation sulfa antibiotics and is widely used in human medicine to treat a number of infections such as urinary tract infections, acute sinusitis, septicemia, nocardiosis [2-3]. The poisoning by these drugs results when swallowed, inhaled, injected, or absorbed percutaneously is capable of causing death, injury, toxic reactions, on of perspective methods for emergency treatment of accidental poisoning by drug is adsorption[4] . Many types of adsorbents such as kaolin, charcoal, polymers, attapuligate, bentonite in adsorption of drug [5]. Adsorption is quite promising due to its high efficiency, easy handling, availability of different adsorbents, simplicity of design and cost effectiveness[6-7] .

Hydrogels are crosslinked hydrophilic polymers that are swollen in water usually to equilibrium in aqueous solution that typically carries a large amount of water while remaining insoluble [8-10] Water absorbing nature of hydrogels is mainly due to the presence of hydrophilic groups such as -CONH2, - CONH-, -OH, -COOH, -SO3H, etc. which are present in the polymer chains[11]. Recently hydrogels have been widely used in many potential application areas such as medicine because of their porous structure and water swellability [12-13] , good biocompatibility with the human body[14] .

Materials and Methods

Instruments

1- UV-Visible spectrophotometer, Double Beam, Shimadzu. PC 1650, Japan.

2-UV-Visible Spectrophotometer, Single Beam, UV -7310, Jenway, UK

2- Electronic Balance, Sartorius Lab. L420 B, +0.0001.

3- Dunboff metabolic shaking Incubater GCA/ precision Scientific.

4- Centrifuge tubes., Hettich Universal (D-7200).

5- pH-meter, pH-3110, Intertek, Germany.

6- Oven, Memort LOD–080N , Jlabtech, Korea .

8- Hotplate-Stirrer, L-81, Jlabtech, Korea .

Materials:

Acryl amide and crotonic acid were supplied by (Himedia, India). The activator N, N, N', N'-tetramethylethylenediamine (TEMED) supplied from Merck(Darmstadt, Germany) and were used as the redox initiator pair, The initiator, potassium persulfate (KPS) was supplied by(merck, Germany) .The multifunctional crosslinker isN,N'-methylene biascrylamide (NMBA) was purchase from (Fluka, Germany). Sodium chloride was obtained from(Fluka, Germany) . Sulfadiazine was purchase from (Sigma-Aldrich, Germany) . Sodium Hydroxide and Hydrocholric acid were supplied from (Fluka, Germany)

Adsorption Isotherm

Solutions of drugs (10ml) of known concentrations (1-50ppm) at pH ≈ 1.2 were added to stoppered flasks containing 0.1g of hydrogel. The flasks were shaken in a thermostatically controlled water bath at a speed of 150 cycle/min. till equilibrium is attained (90 min for Sulfadiazine and 120 min for Sulfathiazole). This time is sufficient for the adsorption process to reach equilibrium. After the equilibrium time elapsed, the suspensions were either centrifuged at 3000 rpm for 10 min. The clear supernatants were assayed for drugs, after appropriate dilution, spectrophotometrically. Equilibrium concentrations were obtained by comparing the experimental data with the calibration curve.

The quantity of drug adsorbed was calculated according to the following equation (1):-

$$Q_e \text{ or } \frac{x}{m} = \frac{V(C_o - C_e)}{m} \quad \text{..... (1)}$$

Where:

x: the quantity adsorbed.

m: weight of adsorbent (g).

$C_{o:}$ initial concentration (mg/L).

C_e: equilibrium concentration (mg/ L).

V: volume of solution (L).

Effect of Temperature

Adsorption experiment was repeated in the same manner at temperatures of 15, 25, 30 and 35 ^{o}C to estimate the basic thermodynamic functions.

Effect of pH

Adsorption experiment was carried out as mentioned previously as a function of pH using a fixed concentration of drugs. Hydrochloric acid was used to adjust the pH range from 1.2 to 11. The pH of the suspensions at the commencement of the adsorption was measured at the end of the experiment using pH-meter.

Effect of ionic strength

The effect of the addition (0.01-0.3g) of sodium chloride to solutions containing fixed concentration of adsorbate equilibrated with 0.1g of adsorbent were investigated under the same experimental conditions described before.

Adsorption of Sulfadiazine

The adsorption of Sulfadiazine from aqueous solution on hydrogels has been studied at 15˚C and at other three temperatures (25, 30 and 35˚C). Table (1) shows the related results by the equilibrium concentration (C_e) and the quantity adsorbed on hydrogels (Q_e). The general shape of Sulfadiazine adsorption isotherms is shown in Figure (1), where the quantities adsorbed on hydrogels is plotted as a function of equilibrium concentration at the above temperatures.

The results showed an increase in adsorptive capacities of hydrogels as the concentration of Sulfadiazine increased until reaching a limited value. Hydrogel was found of reasonable surface activity in adsorption from solution of some materials and drug.

Table (1) Amounts of Sulfadiazine uptake by hydrogel from aqueous solution at different temperatures

	15 ˚C		25 ˚C		30 ˚C		35 ˚C	
Sulfadiazine drug	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
	0.804	0.019	0.695	0.030	0.75	0.025	0.677	0.032
	2.830	0.216	2.666	0.233	2.830	0.216	2.994	0.200
	5.184	0.481	5.056	0.494	5.202	0.479	5.239	0.476
	10.038	0.996	9. 819	1.018	9.947	1.005	10.713	0.928
	12.063	1.293	12.939	1.206	12.994	1.200	13.122	1.187
	14.125	1.587	14.217	1.578	14.271	1.572	14.454	1.554
	15.220	2.477	17.009	2.299	18.463	2.153	18.979	2.102
	20.403	2.959	22.063	2.793	22.483	2.751	23.085	2.691

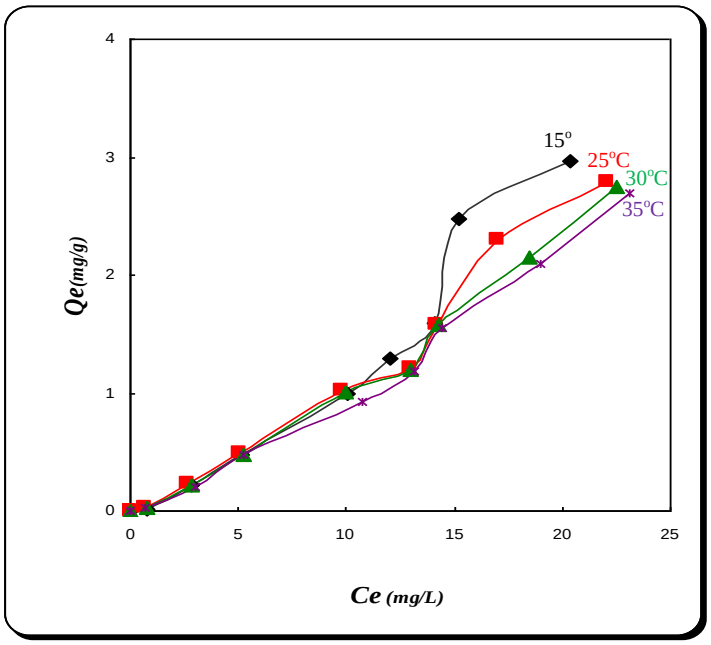

Figure (1) Adsorption isotherms of Sulfadiazine on hydrogel at different temperatures (^{o}C)

In acrylamide-co-crotonic acid croos-linked an atom of lower positive valence replaces one of higher valence, resulting in a deficit of positive charge, or in other words, an excess of negative charge. This excess of negative layer charge is externally compensated by the adsorption on the layer surfaces of cations, which are too large to be accommodated in the interior of the crystal. In aqueous solution, the compensating cations on the layer surfaces may easily be exchanged by other cations when available in solution [15]. The inner one consisting of negative charges and the outer one containing the positive ions; this concept is known as electrostatic double layer. This fact means the hydrogel particles in aqueous solution are charged and can attract molecules either by electrostatic forces, for the oppositely charged molecules, or by inducing dipole formation in the neutral molecule.

The shapes of Sulfadiazine adsorption isotherms were found to coincide with the S-type isotherm reported by Giles classification [16]

The S-type isotherm depends upon the Freundlich assumption about the heterogeneity of the surface. Heterogeneity is a usual and a general feature of surface properties due to different unsaturated adsorption sites of different energetic behaviour. The isotherm S-shaped, probably corresponds to electrostatic adsorption of one layer, followed by adsorption of second layer by van der waals attraction[17-19].

The experimental adsorption data were applied to both the empirical Freundlich, Timken equation and the theoretical Langmuir isotherm equation. These results indicated the applicability of Freundlich isotherm as shown by the linear relationships of (log Q_e) versus (log C_e) (Table (2) and Figure (2)).

Table (2) Amounts of Sulfadiazine uptake by hydrogel at 15 °C with the proper calculations for the application of Freundlich equation

Sulfadiazine drug	*Langmuir equation*			*Freundlich equation*			*Timken equation*		
	K_L	q_m	R^2	K_F	n	R^2	K_T	b	R^2
	-	-	0.4255	0.034	0.673	0.9839	0.657	0.795	0.7436

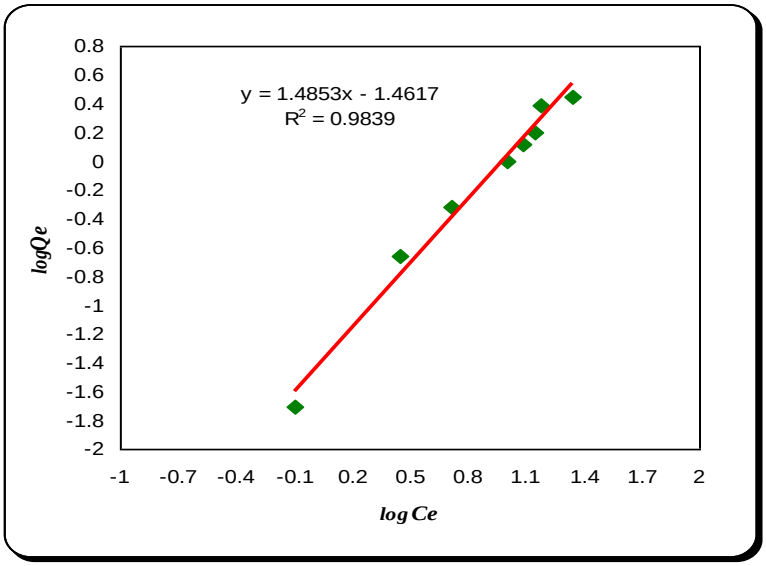

Figure (2): Linear form of Freundlich isotherm of Sulfadiazine on hydrogels

The influence of pH on the adsorption extent of Sulfadiazine was investigated upon using pH solutions (pH =1.2-11). Table (3) and Figure (3) demonstrate the effect of pH on the adsorption uptake of a fixed drug concentration by hydrogels at 15˚C.

Table (3): Amounts of Sulfadiazine uptake by hydrogels at 15°C from solutions of different pH values

Sulfadiazine Drug	C_o *(mg/L)*	pH	Q_e (mg/g)
	25	1.2	1.580
	25	3	1.522
	25	4	1.438
	25	6	1.288
	25	8	1.204
	25	9	1.173
	25	11	1.151

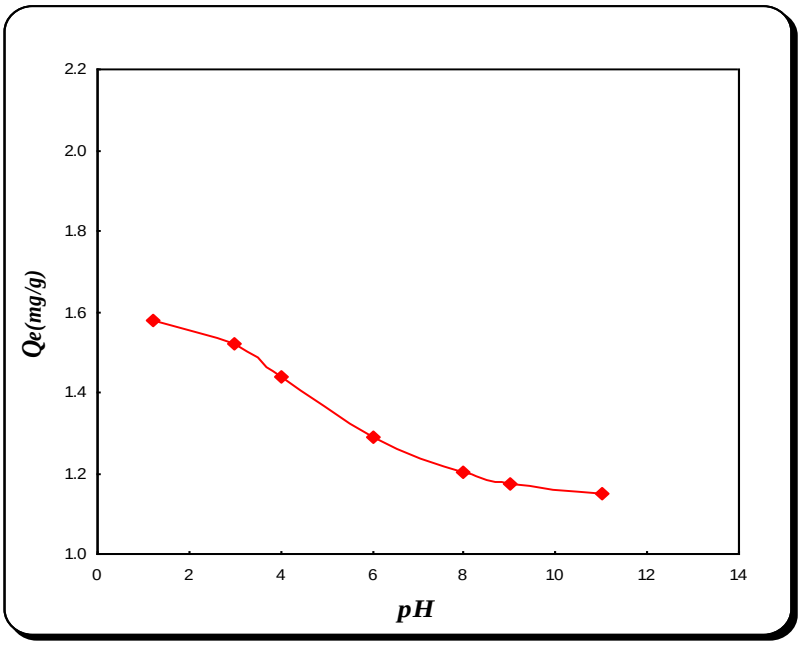

Figure (3): Effect of pH in adsorption uptake of Sulfadiazine on hydrogel at 15°C

The results showed an decrease in adsorption quantities of the drug on hydrogels with increasing pH value (Table (3) and Figure (3)). In this study, hydrogels was presumed to carry a negative charge and Sulfadiazine is amphoteric in nature and may primarily exist as cationic, neutral, and anionic species, based on the pH of the aqueous phase. At low pH ($pH<pK_{a1}$), sulfadiazine exists as a cationic species due to the dissociation of the ammonium group($-NH3^{+}$) , hence occurs electrostatic attraction between positive charges of sulfadiazine and negative charges of hydrogels, resulting in increasing adsorption at low pH [20] .

The effect of temperature variation on the adsorption extent of drug on hydrogels has been studied. The data and the general shapes of Sulfadiazine adsorption isotherms at four different temperatures are given in Table (1) and Figure (1). The quantities of sulfadiazine adsorbed on hydrogels decreased with increasing temperature, The increase in temperature may increase the solubility of the solute, hence decreasing its adsorption affinity towards the surface, in addition, to the increase in the kinetic energy of the species. Consequently, there is an increase in the entropy of the system, which results in a decrease of aggregate organization on the surface of the adsorbent [21,22] .

The basic thermodynamic quantities of adsorption of Sulfadiazine on the hydrogels were estimated through calculating X_m values at different temperatures .The heat of adsorption (ΔH) may be obtained from Van't Hoff equation :$\ln x_m = -\Delta H/RT + \text{constant}$, the change in free energy (ΔG) could be determined from equation : $\Delta G = -RT\ln K_{eq}$ and the change in entropy (ΔS) was calculated from Gibbs equation: ($\Delta G = \Delta H - T.\Delta S$)

Table (4) and Figure (4) demonstrate these calculations.

Table (4) Effect of temperature on the maximum adsorbed quantity for adsorption of Sulfadiazine on the hydrogels at C_e = 22.228

Sulfadiazine drug	T °C	T K	1000/T K^{-1}	C_e = 22.2281	
				X_m	ln X_m
	15	288	3.472	2.777	1.021
	25	298	3.355	2.7	0.993
	30	303	3.300	2.65	0.974
	35	308	3.246	2.575	0.945

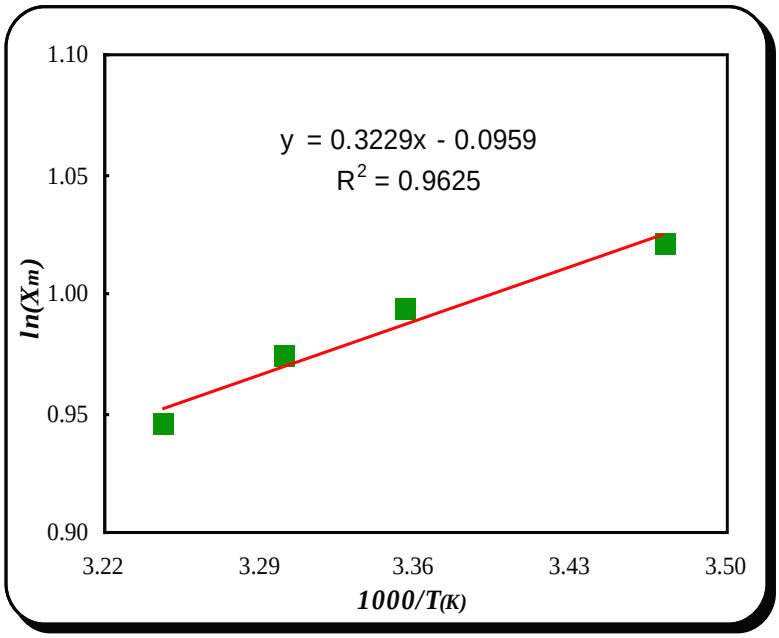

Figure (4): Plot of ln X_m against reciprocal absolute temperature for adsorption of Sulfadiazine on the hydrogels

Table(5)shows the basic thermodynamic values of adsorption of Sulfadiazine on the hydrogels. The interaction between Sulfadiazine and the hydrogels exhibited low enthalpy values. An adsorption of van der Waals type is suggested to take place as indicated by these values.

Table (5) Values of thermodynamic functions of adsorption process of Sulfadiazine on the hydrogels at 15 °C

Drug	ΔH (kJ.mol^{-1})	ΔG (kJ.mol^{-1})	ΔS (J.$mol^{-1}.K^{-1}$)	Equilibrium Constant (k)
Sulfadiazine	−2.684	−2.117	−1.873	2.429

The negative value of the ΔH for the adsorption of sulfadiazine on hydrogels at at 15 ^{o}C indicated that the adsorption was an exothermic process and **Δ**H value were < 20 kJ mol^{-1} so adsorption process is a physical adsorption [23]. The negative value of the ΔG for the adsorption of sulfadiazine on hydrogels indicated that the adsorption process is spontaneous. The negative value of ΔS for the adsorption of sulfadiazine on hydrogels at 15 **º**C indicated a decrease in the degree of freedom of the adsorbed species [24].

Influence of ionic strength on the drug adsorption on hydrogels surface

The effect of ionic strength on adsorption uptake of sulfadiazine drug on adsorbent surface was studied at variable salt weights (0.01–0.3gm) of sodium chloride. As can be seen in Table (6) and Figure (5), the increasing ionic strength in the solution causes an increased in the adsorption of sulfadiazine drug on hydrogels surface at the 15^{o}C. This behavior may be due to the reduction in adsorbate solubility as a result of higher interaction of electrolyte ions with the aqueous solvent, the solubility of ionic salts in aqueous media is normally higher than that of organic drug molecules, therefore, a competition between them to interact with the solvent molecules leads to an increase in the attraction between the hydrogels surface and the drug molecules which in turn will decrease the solvent – drug interaction [25].

Table (6): Amounts of Sulfadiazine uptake by hydrogels at 15^{o}C from solutions at different weights of NaCl

	C_o *(mg/L)*	wt in gm of NaCl	Qe (mg/g)
Sulfadiazine Drug	25	0	1.293
	25	0.01	1.315
	25	0.05	1.328
	25	0.1	1.344
	25	0.15	1.388
	25	0.2	1.434
	25	0.25	1.481
	25	0.3	1.496

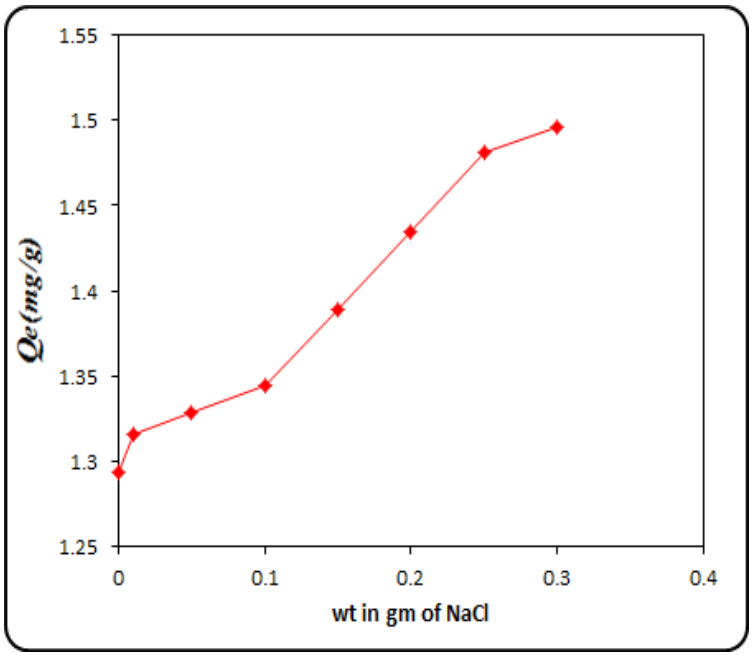

Figure (5): Effect of ionic strength on adsorption of Sulfadiazine on hydrogels at 15°C

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