The Adsorptive Removal of Sulfadiazine Drug from Aqueous Solution Using Poly (Acryl Amide-co-Crotonic Acid) Hydro Gels

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Abstract

The adsorption of Sulfadiazine drug from aqueous solution has been investigated using acryl amide-co-crotonic acid cross-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 showed greater adsorption uptake of the Sulfadiazine than Sulfathiazole on the hydro gels. The adsorption phenomenon was examined as a function of temperature (15, 25, 30 and 35°C). The extents of adsorption of drug on the hydro gels were found to decrease with increasing temperature (exothermic process). The basic thermodynamic functions have also been calculated. Adsorption on hydro gels 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, Hydro gels, 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, one of perspective methods for emergency treatment of accidental poisoning by drug is adsorption[4].

Many types of adsorbents such as kaolin, charcoal, polymers, attapulgite, bentonite in adsorption of drug [5]. Adsorption is quite promising due to its high efficiency, easy handling, availability of different adsorbents, and simplicity of design and cost effectiveness [6-7].

Hydro gels are cross linked 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 hydro gels 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 hydro gels have been widely used in many potential application areas such as medicine because of their porous structure and water swell ability [12-13], good biocompatibility with the human body [14].

Materials and Methods

Instruments

- UV-Visible spectrophotometer, Double Beam, Shimadzu. PC 1650, Japan.
- UV-Visible Spectrophotometer, Single Beam, UV-7310, Jenway, UK
- Electronic Balance, Sartorius Lab. L420 B, +0.0001.
- Dunboff metabolic shaking Incubator GCA/ precision Scientific.
• Centrifuge tubes. Hettich Universal (D-7200).

• Ph-meter, pH-3110, Intertek, Germany.

• Oven, Memort LOD–080N, Jlabtech, Korea.

• 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 per sulfate (KPS) was supplied by (merck, Germany) .The multifunctional cross linker is N, N'-methylene bisacrylamide (NMBA) was purchase from (Fluka, Germany). Sodium chloride was obtained from (Fluka, Germany). Sulfadiazine was purchase from (Sigma-Aldrich, Germany). Sodium Hydroxide and Hydrochloric 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 0.1 g of hydrogel.

The flasks were shaken in a thermostatically controlled water bath at a speed of 150cycle/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):

\[ Q_e = \frac{x}{m} \frac{V(C_o - C_e)}{m} \] ..............................(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 °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 hydro gels 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 hydro gels (Q_e). The general shape of Sulfadiazine adsorption isotherms is shown in Figure (1), where the quantities adsorbed on hydro gels is plotted as a function of equilibrium concentration at the above temperatures. The results showed an increase in adsorptive capacities of hydro gels as the concentration of Sulfadiazine increased until reaching a limited value. Hydro gel was found of reasonable surface activity in adsorption from solution of some materials and drug.
Table 1: Amounts of Sulfadiazine uptake by hydro gel from aqueous solution at different temperatures

<table>
<thead>
<tr>
<th>Sulfadiazine drug</th>
<th>C_e (mg/L)</th>
<th>Q_e (mg/g)</th>
<th>C_e (mg/L)</th>
<th>Q_e (mg/g)</th>
<th>C_e (mg/L)</th>
<th>Q_e (mg/g)</th>
<th>C_e (mg/L)</th>
<th>Q_e (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°C</td>
<td>0.804</td>
<td>0.019</td>
<td>0.695</td>
<td>0.030</td>
<td>0.75</td>
<td>0.025</td>
<td>0.677</td>
<td>0.032</td>
</tr>
<tr>
<td></td>
<td>2.830</td>
<td>0.216</td>
<td>2.666</td>
<td>0.233</td>
<td>2.830</td>
<td>0.216</td>
<td>2.994</td>
<td>0.200</td>
</tr>
<tr>
<td>30°C</td>
<td>5.184</td>
<td>0.481</td>
<td>5.056</td>
<td>0.494</td>
<td>5.202</td>
<td>0.479</td>
<td>5.239</td>
<td>0.476</td>
</tr>
<tr>
<td></td>
<td>10.038</td>
<td>0.996</td>
<td>9.819</td>
<td>1.018</td>
<td>9.947</td>
<td>1.005</td>
<td>10.713</td>
<td>0.928</td>
</tr>
<tr>
<td></td>
<td>15.220</td>
<td>2.477</td>
<td>17.009</td>
<td>2.299</td>
<td>18.463</td>
<td>2.153</td>
<td>18.979</td>
<td>2.102</td>
</tr>
<tr>
<td></td>
<td>20.403</td>
<td>2.959</td>
<td>22.063</td>
<td>2.793</td>
<td>22.483</td>
<td>2.751</td>
<td>23.085</td>
<td>2.691</td>
</tr>
</tbody>
</table>

Figure 1: Adsorption isotherms of Sulfadiazine on hydrogel at different temperatures (°C)

In acrylamide-co-crotonic acid cross-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 hydro gel 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 behavior.

The isotherm S-shaped probably corresponds to electrostatic adsorption of one layer, followed by adsorption of second layer by Vander 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).
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 hydro gels at 15°C. The results showed a decrease in adsorption quantities of the drug on hydro gels with increasing pH value (Table (3) and Figure (3)). In this study, hydro gels 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 (\(\cdot\text{NH}_3^+\)) hence occurs electrostatic attraction between positive charges of sulfadiazine and negative charges of hydro gels, resulting in increasing adsorption at low pH [20]. The effect of temperature variation on the adsorption extent of drug on hydro gels 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 hydro gels 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 hydro gels were estimated through calculating \(X_m\) values at different temperatures. The heat of adsorption (\(\Delta H\)) may be obtained from Van't Hoff equation: \(\ln X_m = -\Delta H/RT + \text{constant}\), the change in free energy (\(\Delta G\)) could be determined from equation: \(\Delta G = -RT\ln K_{eq}\) and the change in entropy (\(\Delta S\)) 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 \(C_e = 22.228\) mg/L

<table>
<thead>
<tr>
<th>Sulfadiazine (Drug)</th>
<th>(T^\circ C)</th>
<th>(\frac{T}{K})</th>
<th>(\frac{1000}{T})</th>
<th>(X_m)</th>
<th>(\ln X_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfadiazine</td>
<td>15</td>
<td>288</td>
<td>3.472</td>
<td>2.777</td>
<td>1.021</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>298</td>
<td>3.355</td>
<td>2.7</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>303</td>
<td>3.300</td>
<td>2.65</td>
<td>0.974</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>308</td>
<td>3.246</td>
<td>2.575</td>
<td>0.945</td>
</tr>
</tbody>
</table>

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

Table 5 shows the basic thermodynamic values of adsorption of Sulfadiazine on the hydro gels. The interaction between Sulfadiazine and the hydro gels exhibited low enthalpy values. An adsorption of Vander 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 hydro gels at 15°C

<table>
<thead>
<tr>
<th>Drug</th>
<th>(\Delta H) (kJmol(^{-1}))</th>
<th>(\Delta G) (kJmol(^{-1}))</th>
<th>(\Delta S) (Jmol(^{-1}).K(^{-1}))</th>
<th>Equilibrium Constant (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfadiazine</td>
<td>-2.684</td>
<td>-2.117</td>
<td>-1.873</td>
<td>2.429</td>
</tr>
</tbody>
</table>

The negative value of the \(\Delta H\) for the adsorption of sulfadiazine on hydro gels at 15 °C indicated that the adsorption was an exothermic process and \(\Delta H\) value were< 20 kJ mol\(^{-1}\) so adsorption process is a physical adsorption [23]. The negative value of the \(\Delta G\)
for the adsorption of sulfadiazine on hydro gels indicated that the adsorption process is spontaneous. The negative value of $\Delta S$ for the adsorption of sulfadiazine on hydro gels at 15 °C indicated a decrease in the degree of freedom of the adsorbed species [24].

Influence of Ionic Strength on the Drug Adsorption on Hydro Gels Surface

The effect of ionic strength on adsorption uptake of sulfadiazine drug on adsorbent surface was studied at variable salt weights (0.01–0.3 gm) 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 hydro gels surface at the 15°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 hydro gels surface and the drug molecules which in turn will decrease the solvent – drug interaction [25].

<table>
<thead>
<tr>
<th>Sulfadiazine Drug</th>
<th>$C_0$ (mg/L)</th>
<th>wt in gm of NaCl</th>
<th>Qe (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>0</td>
<td>1.283</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.01</td>
<td>1.315</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.05</td>
<td>1.328</td>
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<tr>
<td></td>
<td>25</td>
<td>0.1</td>
<td>1.344</td>
</tr>
<tr>
<td></td>
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<td>0.15</td>
<td>1.388</td>
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<tr>
<td></td>
<td>25</td>
<td>0.2</td>
<td>1.434</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.25</td>
<td>1.481</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.3</td>
<td>1.496</td>
</tr>
</tbody>
</table>

Figure 5: Effect of ionic strength on adsorption of Sulfadiazine on hydro gels at 15°C

References

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