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Synthesis, characterization and properties of hydrogel based on acrylic acid composite for removal of cadmium ion from wastewater

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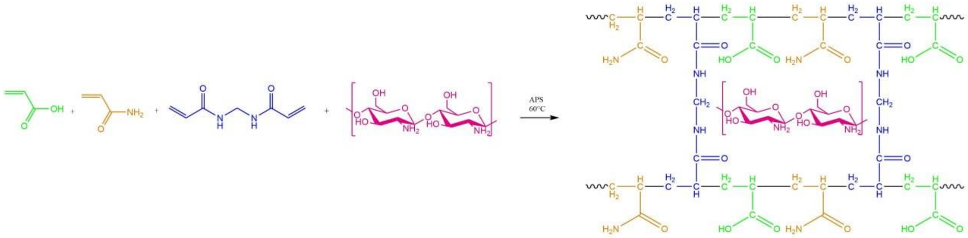
Abstract: The hydrogel of Poly (Acrylic Amide - Acrylic Acid)/ Chitosan (PAM-AA/CTS) synthesized via free radical polymerization of Acrylamide and acrylic acid as monomers also added chitosan, using MBA as a cross-linking agent and KPS as initiator at 60 °C. FTIR and TGA spectroscopy were used to characterize the hydrogel. The FTIR results before and after absorbing Cd (II) reveals the presence of a broad absorption band in the range of 3190 - 3513 cm-1, where the O–H band overlaps with the N–H band, shows the presence of carboxylic and amines functional groups. Additionally, bands between 1743 and 1679 cm-1 suggest the presence of carbonyl bonds, and also, the sample was heated under an atmosphere with 10 °C. min-1 between 25 °C and 1000 °C. Though heating the hydrogel in ranges from 270-430 °C causes 50% mass loss that may be due to the pyrolysis of the carboxylic acids and amines groups. Hydrogel composed of PAM-AA/CTS efficiently removes heavy metals from aqueous solutions. Using the isotherm models of the Langmuir and Freundlich and those findings indicates that the potential is relatively high; however, the Langmuir equation does detect a good correlation with the Cd2+ ion. The maximum sorption capacity was determined to be 31.5 mg/g. Langmuir isotherm provided the best explanation for the current outcome. Thermodynamic analysis shows that the adsorption of Cd2+ is endothermic. These results show that hydrogels are effective, affordable, and ecologically acceptable materials for removing Cd2+ ions from aqueous solutions.

Keywords: Synthesis, Hydrogel, Adsorption, Free radical polymerization, Cadmium ion.

Introduction

For organic chemists, the synthesis of hydrogel molecules is a complicated subject to work on (for a few examples of hydrogel synthesis, see [1]). Free radical polymerization, a reaction between acrylic and maleic acid that has been reported, is a very effective technique in this sector. This is a legitimate one-pot for creating hydrogel from widely available raw ingredients (Scheme **1**).



Scheme 1. Synthesis of Hydrogel based on acrylic acid

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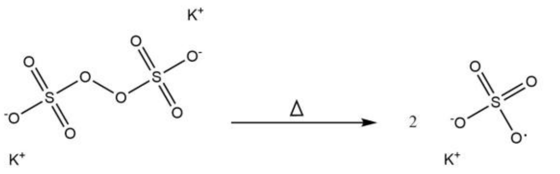
Free-Radical Polymerization

Initiators

Free radicals are created during the potassium persulfate's thermal breakdown. The process of heat breakdown is depicted in Scheme **2**.



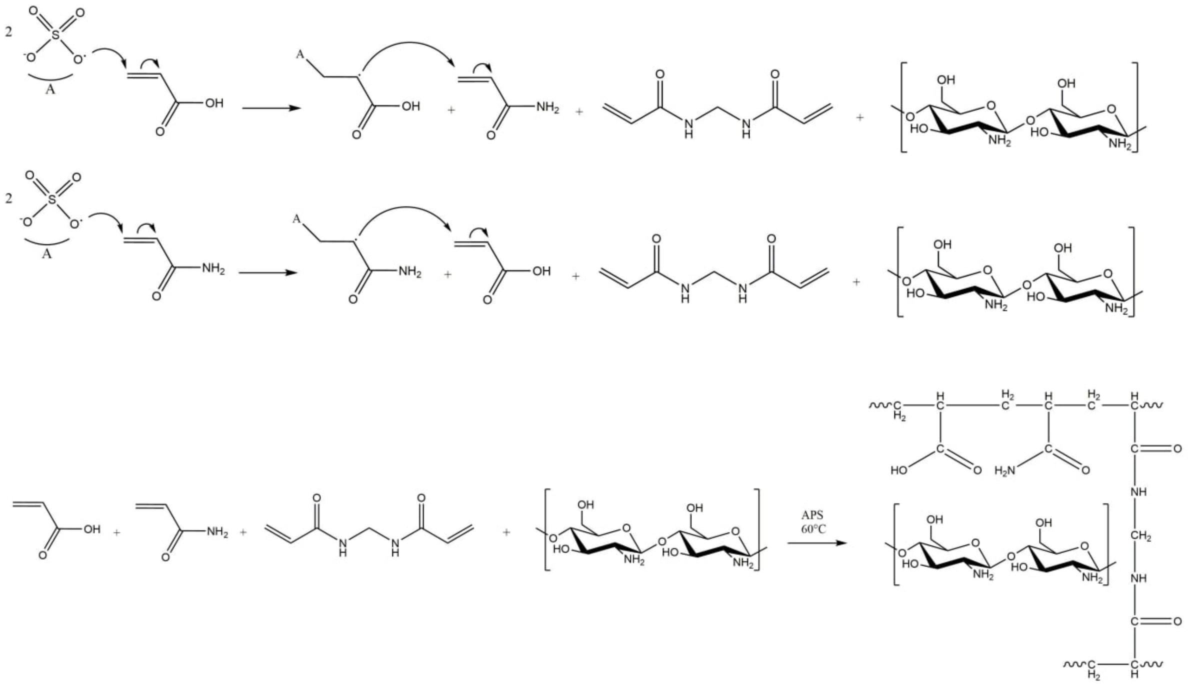
Scheme 2. Decomposition behaviour of potassium persulphate initiator at 60 °C temperatures

Propagation

"Propagation" comes after "initiation." The radical site at the initial monomer unit attacks the double bond of a new monomer molecule during the propagation stage. As a result, the second monomer unit is linked to the first, and the radical site is transferred from the first monomer unit to the second by unpaired electron transfer.

It should be observed that this chain still has a radical site (shown by a dot) at the carbon atom at the end and may, thus, attack and take on yet another monomer molecule while also transferring the radical site to the newly added monomer unit.

This process entails a constant assault on brand-new monomer molecules, which keep adding to the expanding chain one by one. The propagation continues until the chain expansion is terminated by a pure termination process, the free-radical site being "killed" by certain impurities, or until there is no more monomer remaining for the assault. According to Scheme **3**.



Scheme 3. Mechanism of preparation of hydrogel

It is generally acknowledged that environmental Pollution generated toxicity is the most severe worldwide issue. Emerging tendencies raise significant scientific and health issues. Pollution wreaks havoc on living beings, the most significant environmental concern [1]. In recent years many academics and experts throughout the globe have been interested in removing several harmful compounds from water and wastewater. Plating, pigment, battery, metallurgy, mining, engineering, dyeing, printing, PVC stabilizers, nuclear power operation, semiconductor, electric industrial applications, and cosmetics are all manufacturing-related industries that contribute a variety of contaminants to wastewater [2]. The only answer would be to remove these compounds from the waste before releasing them into the environment.

Moreover, eliminating inorganic and organic harmful chemicals from the mushroom industry would have significant ecological significance due to their ubiquity and toxicity. Heavy metals have been identified as a part of the most severe environmental issues. It is recognized that heavy metal in aquatic environments poses several health risks to animals and people [3]; such metals have polluted a large region due to their presence in pesticides, communal sludge waste, fertilizers, mining residues, and smelting operations. Heavy metals are carcinogenic and, due to their permanence accumulation and indestructibility, may represent one of the most significant risks to living beings [4, 5]; even so, some heavy metals are essential to existence and play an irreplaceable part in the metabolic process of humans, such as the functioning of essential enzyme sites nonetheless their excessive amounts may be hazardous to organisms [6] Our effort entails determining the adsorption capacity of PAM-AA/CTS for Cd^{2+} from an aqueous solution under varying concentration settings and calculating the isotherm parameters under these conditions.

Results and discussion

Hydrogel composition

The hydrogel was synthesized by free radical polymerization of MBA as a cross-linking agent and $k_2S_2O_8$ as an initiator at 60 °C. FTIR and TGA spectroscopy characterized the hydrogel, as shown in Figures 1 and 2. The infrared spectrum of hydrogel before and after the absorption of heavy metal shown in Figure 1 reveals the presence of a broad absorption band in the range of 3190-3513 cm^{-1} where the O–H band overlaps with the N–H band. Additionally, bands between 1743 and 1679 cm^{-1} suggest the presence of carbonyl bonds (C = O) [7-9]. To study the hydrogel's thermal stability, the sample was heated under an atmosphere with 10 °C min^{-1} up to 1000 °C. Therefore, heating P (CH /AA-co-AM) resulted in a weight loss of up to 57 % in ranges between 75 °C and 210 °C because of moisture. However, heating the composite in ranges from 270-430 °C causes 50% mass loss that may be caused by pyrolysis, resulting in the breakage of the chemical bonds into the polymeric chains as well as declined polymerization degree and removed hydroxyl and carboxyl groups in the form of CO_2 and CO. Furthermore, it removed amide and amine groups It was found that the hydrogel lost 11.50% of the weight in a thermal range between 360 °C and 650 °C that may be caused by thermal breakage of the polymeric chains of the hydrogel as appear in Figure 2. Hydrogel PAM-AA/CTS can be used as a suitable adsorbent for effective elimination of Cd^{2+} ions in wastewater as it was shown in Figure **3**. This may be because of the inclusion of chitosan, which increases the absorption capacity of PAM-AA/CTS hydrogel through the carboxylic and amine groups.

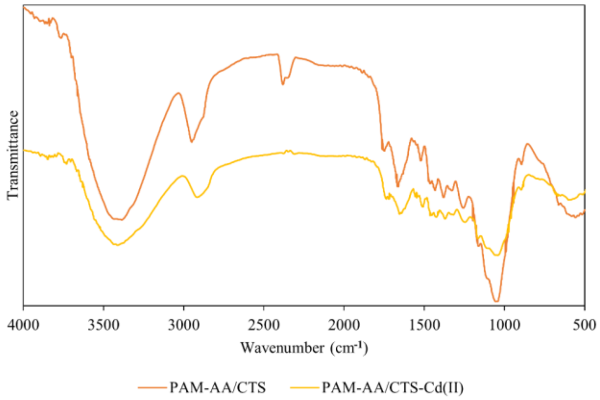


Figure 1. FTIR spectra of PAM-AA/CTS hydrogel before and after adsorption of Cd^{2+}

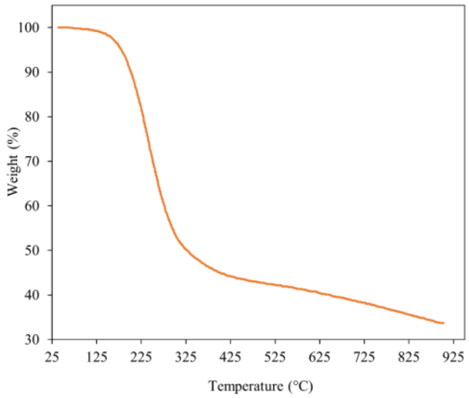


Figure 2. TGA measurements of PAM-AA/CTS hydrogel

Effects of contact time

Figure **3** depicts the influence of contact time on the adsorption of Cd^{2+} ions on PAM-AA/CTS. The results indicate that the adsorption technique achieves equilibrium in one hour, and the adsorption capacity of Cd^{2+} rises with increasing contact time. During the first 5 minutes of contact, PAM-AA/CTS absorbed more than 7.11 mg/g of Cd^{2+} ions; changes in sorption capacity after 5 minutes were relatively moderate and reached equilibrium after 1 hour with 17.02 mg/g of Cd^{2+} ion [11,12].

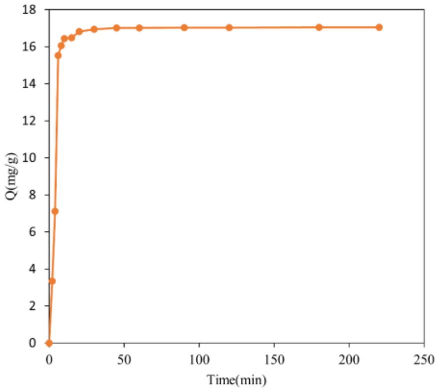


Figure 3. Adsorption capacity of PAM-AA/CTS hydrogels for Cd2+ (initial metal ion concentration = 10 mg/L)

The influence of pH

The effect of pH solution on the adsorption of Cd^{2+} ions on the hydrogel depended on the concentration of Cd^{2+} ions, which was 10 mg/L at 25 °C,160 rpm, and pH was in the range of 2.7 to 9.2 is shown in Figure 4 along with the 1-hour contact time and adsorbent weight was 0. 01 g. Therefore, the adsorption capacity increases as the pH of the solution rise, and the optimal adsorption capacity is seen at pH = 9.2 [13,14]. While at lower pH levels between 2.7 and 5.5, the protonation activity OH predominates and causes the absorbent surface to become negatively charged, resulting in a repulsion interaction between Cd^{2+} ion and Cd^{2+} ion molecules and repulsion between Cd^{2+} ion and the surface of the hydrogel [14-17].

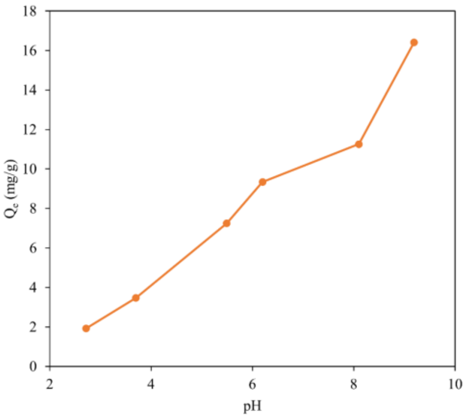


Figure 4. Impact of pH on the absorption of Cd (II) ion on the adsorbent surface PAM-AA/CTS (T = 25 °C, mass adsorbent 0.01 g).

The influence of temperature

Endothermic adsorption is a component of the adsorption of molecules with an increase in temperature that is firmly separated from the surface adsorbent. The temperature of the solution is crucial for the adsorption technique; the influence of the solution temperature is shown for a range of temperatures 10-30 °C in Figure 5. Breaking apart many active functional groups on a hydrogel surface may also result in higher temperatures in equations the thermodynamic variables enthalpy (ΔH°), (ΔG°), Gibbs free energy, and entropy (ΔS°) were calculated from equations 1 and 2 [18]

$$\ln \mathbf{X_m} = \frac{-\Delta \mathbf{H}}{\mathbf{RT}} + \mathbf{constant} \quad (1)$$

$$\Delta G = -RT\ln K \quad (2)$$

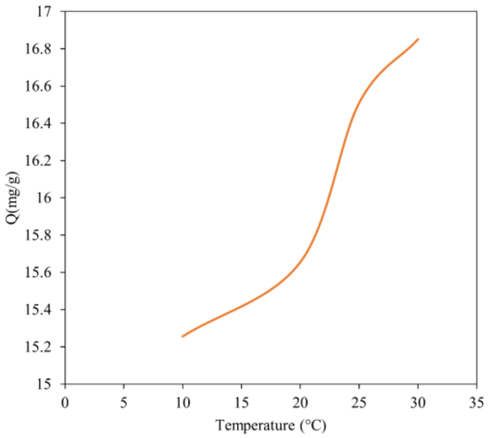


Figure 5. Effect of temperature on adsorption of Cd^{2+} by PAM-AA/CTS hydrogel (initial metal ion concentration = 10 mg/L).

These estimates are shown in Figure 6, and the computed values of Cd^{2+} ions adsorption thermodynamic factors on PAM-AA/CTS are shown in Table 1. The enthalpy value reveals the endothermic absorption technique of Cd^{2+} ions. In order to absorb Cd^{2+} ions, these molecules must shed a portion of their hydrated shell; consequently, energy is required to dehydrate Cd^{2+} ions and the adsorbent surface [14,19-21]. Consequently, the dehydration process sub-endothermic absorption techniques Due to the diffusion of Cd^{2+} ions in sorbent chemical structures [22, 23] positive ΔS and minimally negative ΔG values have been explored.

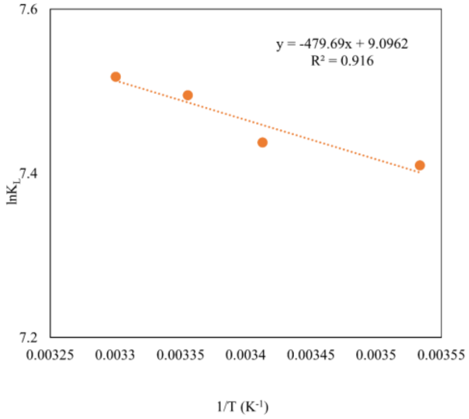


Figure 6. The plot of $\ln K_L$ versus $1/T$ for the adsorption of Cd^{2+} ions (initial concentrations: 10 mg/L, adsorption time: 1 h)

Table 1. Adsorption thermodynamic parameters for Cd^{2+} adsorption by PAM-AA/CTS hydrogel

ΔG (kJ/mol)				**ΔH (kJ/mol)**	**ΔS (J/mol.K)**	**R^2**
283 K	293 K	298 K	303 K			
-17.433	-18.117	-18.569	-18.937	3.988	75.625	0.916

Adsorption isotherm

Freundlich isotherm

The Freundlich equation, which specifies the physical adsorption of a liquid, is one of the straightforward regression methods often used to express adsorption data. Here we provide the empirical Freundlich derivation [24,25]

$$q_e = K_f C_e^{1/n} \qquad (3)$$

Therefore, q_e denotes the quantity absorbed per unit weight of adsorbent at equilibrium (mg/g), (mol/g) Ce indicates the equilibrium concentration of adsorbent in the solution after absorption (mol/L), K_f represents the experimental Freundlich constant or the capacity factor (L/gm) 0.1/n: it has a Freundlich exponent.

Langmuir isotherm

The Langmuir isotherm absorbs contaminants from liquid solutions extensively [26,27]. Another of the equations is derived from Langmuir based on a particular example of the structure of the solution absorption process. Then the Langmuir adsorption isotherm with the assumption [28,29] is shown. In this equation, the Langmuir adsorption isotherm is defined as 4

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \qquad (4)$$

Table 2. Constants of Langmuir and Freundlich isotherm models for Cd^{2+}

Langmuir					**Freundlich**				
R^2	**q$_{max}$**	**K$_L$**	**RMSE**	**Δq$_e$%**	**R^2**	**K$_F$**	**n**	**RMSE**	**Δq$_e$%**
0.999	38.911	0.087	0.350	1.821	0.957	8.224	2.810	0.947	4.735

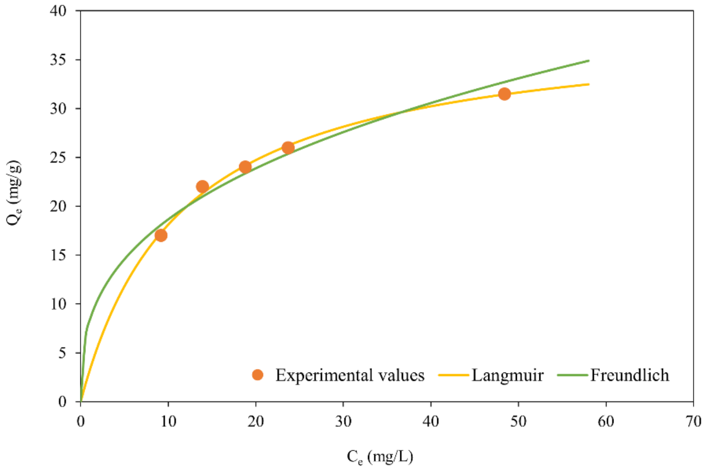


Figure 7. Langmuir, Freundlich and Temkin adsorption isotherms of Cd^{2+} by PAM-AA/CTS

Figure 7 and Table 2 exhibit the parameter values of our model as determined by the plot of q_e versus C_e. Here, q_e is the equilibrium adsorbed quantity per unit of weight of the adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbent in the solution after adsorption (mg/L), and q_0 is the experimental Langmuir constant representing the most significant capacity Absorption (mg/g). In addition, K_F indicates the experimental Freundlich constant, and the Langmuir isotherm model is the best match for the adsorption of Cd^{2+} ions on the hydrogel, as evidenced by the R^2 value 0.999.

Conclusion

This work used a complete preparation of hydrogel (AA-co-AM/CH) which was synthesized by free radical polymerization. FTIR and TGA spectroscopy characterized the hydrogel very well, and also the infrared spectrum of hydrogel before and after the absorption of heavy metal was explained. Also, the thermal stability of the hydrogel was appropriately discussed. It is an efficient adsorbent for toxic ions in an aqueous solution. The evidence points to a hydrogel with increased activity PAM-AA/CTS hydrogel, regarded as the desired system, has several qualities, including inexpensive adsorbent environmental safety and Cd^{2+} removal capability. In the current investigation, complete model isotherm data were used; however, Langmuir provided the most significant correlation for Cd^{2+} ions on the hydrogel $R^2 = 0.9999$. In addition, there was an inverse relationship between adsorbent consumption and hydrogel adsorption efficiency, while adsorption efficiency and initial Cd^{2+} ion concentration rose simultaneously

Experimental

Materials and methods

The analytical quality acrylamide (AM), acrylic acid (AA), potassium persulfate (APS) initiator, and N, N-methylene bis acrylamide (NMBA) cross-linker were acquired from Merk and Chitosan with a deacetylation degree of 96% was purchased from Sigma-Aldrich. They were used without any further purification. All solutions were produced in deionized water. Additionally, Cadmium (II) nitrate was obtained from Sigma-Aldrich.

Synthesis of PAM-AA/CTS

Two sets of the solution were made; the first was made by adding 12 grams of acrylic acid (AA) to sodium hydroxide. Then 12 grams of acrylamide (AM) dissolved in 20 milliliters of water is combined with MBA 0.1 grams in 10 mL water. The solution is stirred for fifteen minutes. The second solution was made by stirring 2 grams of chitosan in 2% acetic acid at 60 °C for 15 minutes. After that, the two sets of solutions were mixed with the addition of KPS 0.15 g in 10 mL water in a nitrogen atmosphere, and the hydrogel was formed within one hour and then dried in a vacuum oven at 60 °C for three hours.

Fourier Transform IR

The hydrogels were structurally characterized using a Fourier Transform infrared spectrometer (Perkin Elmer, USA). Characterization was done before and after the absorption of metal ions on the hydrogel, and also hydrogel spectra were taken to identify the interaction between the hydrogel and metal ions.

Thermal Gravimetric analysis

A thermogravimetric analyzer TGA2 (Mettler Toledo, Switzerland) is used to examine the hydrogel's heat stability with and without absorbed Cd^{2+}. A sample of 0.007 g was put in a platinum cup at temperatures ranging from 25 to 1,000 °C at a rate of 10 °C/min in an atmosphere environment at a 100 mL/min flow rate.

Removing of Cd^{2+}

Around 0.01 g of hydrogel with a length of 0.1 cm immersed in 200 mL of known concentration of cadmium solutions. At specified intervals, a predetermined volume of the solution was removed to analyze the metal concentration until equilibrium was attained.

Adsorption studies

Studies on the adsorption of Cd^{2+} ions have been conducted in batches to evaluate the influence of numerous factors, including pH, temperature, initial concentration of Cd^{2+} ion, and contact time of the solution, while examining the adsorption isotherm model of the processes. Various concentrations of Cd^{2+} ion solutions were produced, and the appropriate quantity of PAM-AA/CTS was added by shaking it in the water bath for 1 hour. The time required to achieve equilibrium circumstances the solutions were filtered, and the filtrate was kept for measuring the Cd^{2+} ion concentration using the graphite furnace atomic spectrometer (Agilent, USA) for dissolved Cd^{2+} in an aqueous solution was determined. We also studied the influence of pH by adjusting the pH of Cd^{2+} ion solutions with HCl and NaOH. To explore the absorption model of isotherms of various concentrations of Cd^{2+} ions in solution was shaken well by an adsorbent until equilibrium was reached. Finally, the absorption capacity and removal % of Cd^{2+} ion by PAM-AA/CTS were estimated by using Eq 7

$$\mathbf{qe} = \frac{\mathbf{Vsol}.(\mathbf{Co} - \mathbf{Ce})}{\mathbf{m}} \tag{7}$$

$$\%\mathbf{E} = \frac{(\mathbf{Co} - \mathbf{Ce})}{\mathbf{Co}}\mathbf{x}100 \tag{8}$$

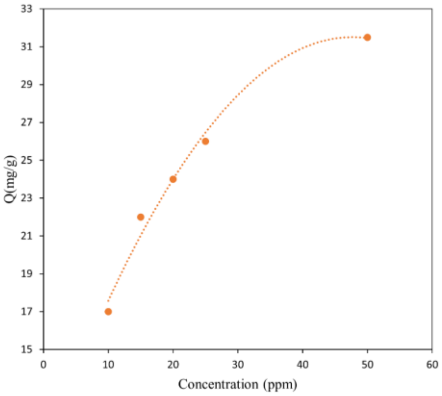


Figure 10. Equilibrium adsorption isotherm of Cd^{2+}

Here q_e (mg. g^{-1}) is the quantity of Cd^{2+} adsorbed at equilibrium by the adsorbent, and C_e (mg. L^{-1}) and C_0 (mg. L^{-1}) are Cd's ion equilibrium and initial concentrations, respectively. Additionally, V (L) is the volume of the additional solution, and m g represents the mass of the adsorbent

Acknowledgements

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