

Uranium Removal from Aqueous Solution Using Starch-Acrylic acid-Acrylamide Hydrogel Prepared by Radiation Technique

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ABSTRACT

Fabrication of Starch-Acrylic acid-Acrylamide hydrogel were accomplished by the use of gamma rays from Co-60 source at room temperature. The adsorbent were characterized by IR. The prepared adsorbent was utilized for absorption of uranium (VI) from aqueous solution. To investigate the effect of adsorption conditions on absorption capacity of the adsorption experiment were executed at changed contact time, pH, temperature and concentration of uranium (VI) solution. Absorption by the adsorbent attains the equilibrium value after 5 hours. pH 3.7 was found optimum considering the highest absorption capacity. The absorption capacity shows highest value at 1000 ppm U(VI) concentration. The absorption capacity achieved under most favorable condition was 166.84 mg/g. Isotherm and kinetic models were used to interpret the U(VI) adsorption mechanism on the hydrogel. Results of desorption of U(VI) ions and reuse of the adsorbent are hopeful. From the study it can be said that the starch-acrylic acid-acrylamide hydrogel adsorbent have potential for uranium (VI) removal from contaminated water.

Keywords: Gamma Radiation; U(VI) adsorbent; Adsorption capacity; Desorption

Introduction

The existence of heavy metal ions in the environment imposes a potential threat due to their detrimental effects not only on human health but also on aquatic and marine environments. Uranium [U(VI)] is one of the heavy metals recognized to be an extremely noxious and nonessential to human and aquatic life [1, 2]. One of the main sources of U(VI) pollution is surface water pollution by the discharge of industrial wastewater since uranium is utilized in a number of industries for instance nuclear reaction, inert gas purification, electronic deoxidant, chemical reagents, production of stained glass and army practice. Environmental threats produced by uranium is not only due to the radioactive effluent from uranium-series radionuclide, but also for the chemical harmfulness of U(VI). Too much ingestion of uranium compound leads to increased risk of cancer, harm to kidney and possible threat to other organs. The World Health Organization has recognized that uranium (VI) is a human carcinogen and its concentration level in water should not go beyond 50mg/L. The U.S. Environmental Protection Agency has suggested a drinking water standard of 20mg/L for ^{238}U [3]. For a number of causes, it is consequently essential to eliminate excess uranyl ions from wastewater. Numerous methods are employed for the elimination of uranium ions from wastewaters and radioactive wastes. Chemical precipitation, ion exchange, solvent extraction, membrane processes, photo catalysis and adsorption are the most frequently used techniques [4–9]. Adsorption of uranium (VI) onto various adsorbents is significant from purification, environmental, and radioactive waste disposal perspective [10, 11].

In recent times hydrogels have presented the potential of adsorption of impurities from polluted water [12]. Hydrogels are a distinct type of super absorbents that can absorb thousands of times of water in excess of their dry weight. They contain cross-linked polymeric chains joined by physical or covalent bonds which produce a three-dimensional network. They have received important consideration in the recent years due to their numerous applications [13–14]. Hydrogel has various usages in fields extending from drug delivery system, self-healing materials, tissue engineering, biosensors, artificial organ generation, hemostasis bandages, biosensors and sorbents for elimination of heavy metals and dyes from wastewater. The hydrophilicity, biocompatibility and high swelling ratio is responsible for the exceptionality of hydrogel from other smart materials. Currently, several types of research are continuing on hydrogel concentrating its application in diverse fields [15–18].

In the present study, Starch-Acrylic acid-Acrylamide hydrogels were produced from their aqueous solution by using gamma radiation. The prepared hydrogels were examined for the adsorption of U(VI) ions. Hydrogels were alkali treated to improve the adsorption of the U(VI) ion. To the best of our knowledge no previous study reported U(VI) adsorption by the starch-acrylic acid-acrylamide hydrogel. In present study, the U(VI) ion adsorption capacity of the alkali-treated hydrogel were studied at different contact times, pH, concentrations and temperature of U(VI) ions. The desorption of U(VI) and reuse of the hydrogel were also carried out.

Experimental

Materials and Reagent

All the chemicals and reagents used in this study were of analytical grade. Acrylic Acid, Acrylamide, Starch, Sodium Hydroxide were purchased from Sigma-Aldrich, Germany. Hydrochloric Acid and Potassium Hydroxide were collected from Merck, Darmstadt, Germany. Uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was supplied by BDH Chemicals Pvt. Ltd., England and Arsenago III was supplied by Fluka, Switzerland.

Instrument and Apparatus

FTIR-ATR investigation in the wavenumber range of 700–4000 cm^{-1} was performed using IRPrestige21 supplied by Shimadzu Corporation, Japan. Various U(VI) ion concentration was analyzed by UV-VIS spectrophotometer (Model: UV2401PC from SHIMADZU, Japan). The irradiation of hydrogel formation was conducted by the Co (60) gamma-irradiator from IFRB, Atomic Energy Research Establishment, Savar, Dhaka, Bangladesh (It was a Panoramic Irradiator of 90 kCi Batch Type collected from BRIT, India).

Synthesis of the poly(Acrylic Acid-co-Acrylamide)-Starch hydrogel

6% starch is taken in distilled water and then stirred to form a paste like slurry. Acrylic acid (5 times of the amount of starch) was poured onto the stirring slurry drop by drop and after that acrylamide (2 times of the amount of starch) was added. A few minutes later, small amount of potassium hydroxide was added bit by bit. The mixture was allowed to be stirred for several minutes to confirm well mixing of all the components. It was then transferred to test tubes covered by poly troughs inside and exposed to 10 kGy gamma radiation. Gamma radiation was applied at a dose rate of 7.22 kGy/h. White, spongy but solid hydrogels were obtained which were cut into small pieces, rinsed well by distilled water and dried naturally. After a month, the hydrogel reached to a constant weight and was stored in a desiccator.

U(VI) absorption by the Starch-Acrylic acid-Acrylamide hydrogel

A constant weight of hydrogel absorbent was kept inside the Uranium (VI) solution in a beaker. Then absorbent started swelling and adsorbing with time. Adsorption were studied by changing contact time, concentration, pH and temperature of U(VI) solution. After adsorption sample concentration before and after absorption was determined by the Arsenazo-III spectrophotometric method [19]. For colour complex formation, 4 mL diluted Uranium (VI) solution was taken into 50 mL volumetric flask and added 0.5 mL 1M HCl, 5 mL 0.01% Arsenago and then filled the volumetric flask up to the mark by distilled water. Then sample concentration was determined by UV-Vis absorption spectroscopy at 652 nm and absorption capacity was calculated. To determine absorption capacity following equation was used:

$$Q = \frac{V \times (C_a - C_b)}{W} \dots\dots\dots(1)$$

Where,

Q= Absorption capacity (mg/g)

V = Volume in L

C_a= Initial concentration (mg/L)

C_b = Final concentration (mg/L)

W = Weight of absorbent (g)

Desorption

Desorption studies can help elucidating the mechanism of an absorption process. Strong acids, such as HCl can desorb the U(VI). 2M HCl solution was used and U(VI) absorbed swollen hydrogel was put into the solution. After 24hr average desorption was calculated by the following equation:

$$\text{Desorption} = \frac{\text{Amount desorbed (mg)} \times 100}{\text{Amount adsorbed (mg)}} \dots\dots\dots (2)$$

Reuse

After desorption, desorbed hydrogel were reverted back to its previous phase by alkali treatment. After alkali treatment, desorbed hydrogel was used to adsorb U(VI) again.

Result and Discussion

Preparation of the poly(Acrylic Acid-co-Acrylamide)-Starch hydrogel

A biodegradable hydrogel is prepared from starch, acrylic acid and acrylamide by radiation technique. The radiation dose used was 10 kGy and dose rate applied was 7.22 kGy/h.

FTIR analysis

Figure 1 shows of the spectrum of the hydrogel. The broader peak at 3300cm⁻¹ signifies –OH group. The presence of =NH may also combine in this region. The peak of 2935cm⁻¹ represents the –CH stretching. The peaks at 1716cm⁻¹ and 1658cm⁻¹ corresponds to the C=O of acrylic acid and acrylamide respectively. The appearance of weak peak at 1716cm⁻¹ and comparatively stronger peak at 1560cm⁻¹ (corresponding to COOK) are noteworthy. It signifies that because of addition of small amount of KOH at the time of synthesis have transformed –COOH group to –COOK that helps to increase the U(VI) adsorption.

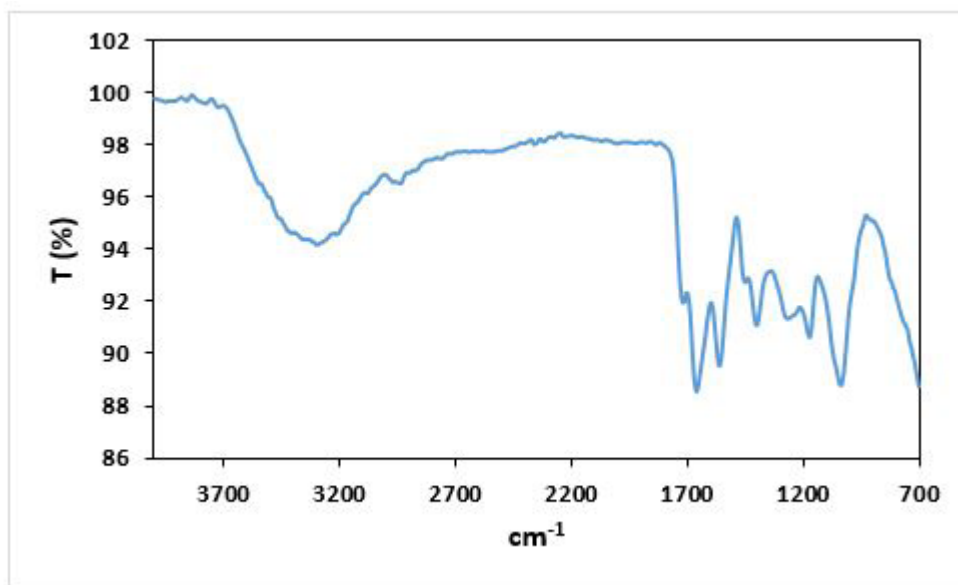


Figure 1: FTIR spectrum of AAc-AAm-Starch hydrogel

U(VI) Adsorption by the Starch-Acrylic acid-Acrylamide hydrogel

The prepared starch-acrylic acid-acrylamide hydrogel were used for adsorption of Uranium (VI) from aqueous solution. The effect of different conditions such as contact time, initial concentration, pH and temperature on adsorption capacity was studied.

Effect of contact time

To know the impact of contact time on adsorption capability, the treated adsorbent were kept in the aqueous solution of Uranium (VI) with constant pH (3.57) having initial Uranium (VI) concentration (100 ppm) at room temperature (30°C). The changes in concentration were measured at regular intervals. The impact of contact time is represented by Figure 2. It is seen that the Uranium (VI) adsorption rate is faster at the beginning and gradually becomes slower near the equilibrium. The equilibrium adsorption of Uranium (VI) reaches after 5 hours contact time. The Maximum adsorption capacity of absorbent was 18.4 mg/g after 5 hours.

The pseudo-first-order rate model equation was stated by Lagergren in 1898 [20]:

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \dots\dots\dots (3)$$

Where Q_e is the quantity of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g), Q_t is the quantity of solute adsorbed at any time (mg/g) and k₁ is the rate constant for the first order adsorption. The stated equation is integrated for the boundary conditions t=0 to t=t and Q=0 to Q=Q and then reorganized to get the equation given below:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \dots\dots\dots (4)$$

This is the most common form of pseudo-first-order kinetic model equation. Pseudo-first-order rate constants can be determined by plotting log (Q_e-Q_t) against t as shown in Figure 3. First-order-kinetics parameters for the uranium (VI) ion adsorption are shown in Table 1. Lagergren equation was reformed by Ho and Mckay and the differential equation is [21]:

$$\frac{dQ_t}{dt} = k_1(Q_e - Q)^2 \dots \dots \dots (5)$$

Integrating the above equation for the boundary conditions $t=0$ and $t=t$ and $Q=0$ to $Q=Q$ and reorganizing to get the linearized form gives the following equation:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \dots \dots \dots (6)$$

This is the most common form of pseudo-second-order kinetic model equation. Here again Q_t and Q_e are the quantity of ions adsorbed (mg/g) at any time and equilibrium time respectively and k_2 (gm/h/mg) is the rate constant for second-order adsorption. The plot of t/Q_t vs. t of the equation should provide a linear relationship as shown in Figure 3 from which k_2 and Q_e can be measured from the slope and intercept of the plot. Pseudo-second-order kinetics parameters were determined and reported in Table 1.

Q_e (experimental) mg/g	Pseudo-first-order rate constant			Pseudo-second-order rate constant		
	Q_e (theoretical) mg/g	k_1 (h ⁻¹)	R ²	Q_e (theoretical) mg/g	k_2 gh ⁻¹ mg ⁻¹	R ²
18.4	13	0.5564	0.9479	20.24	0.005953	0.9902

Table 1: The pseudo-first-order and pseudo-second-order rate constants for U(VI) ion adsorption

From the outcomes, it can be detected that the experimental Q_e value and the theoretical Q_e value calculated from first-order kinetic model are not matching with each other. On the other hand, it can be observed that the experimental Q_e and the theoretical Q_e value calculated from second-order kinetic model consequently agrees with each other. Thus the pseudo-second-order equation is suitable to interpret U(VI) adsorption by the hydrogel.

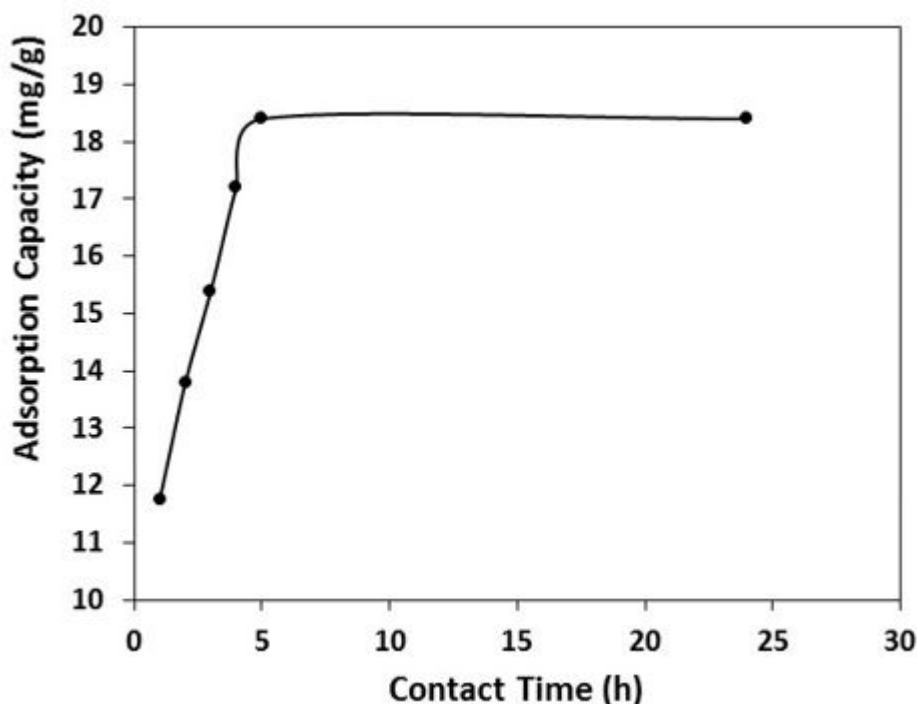


Figure 2: Effect of contact time on adsorption capacity by starch acrylic acid-acrylamide hydrogel (pH 3.57 and concentration 100 ppm at room temperature)

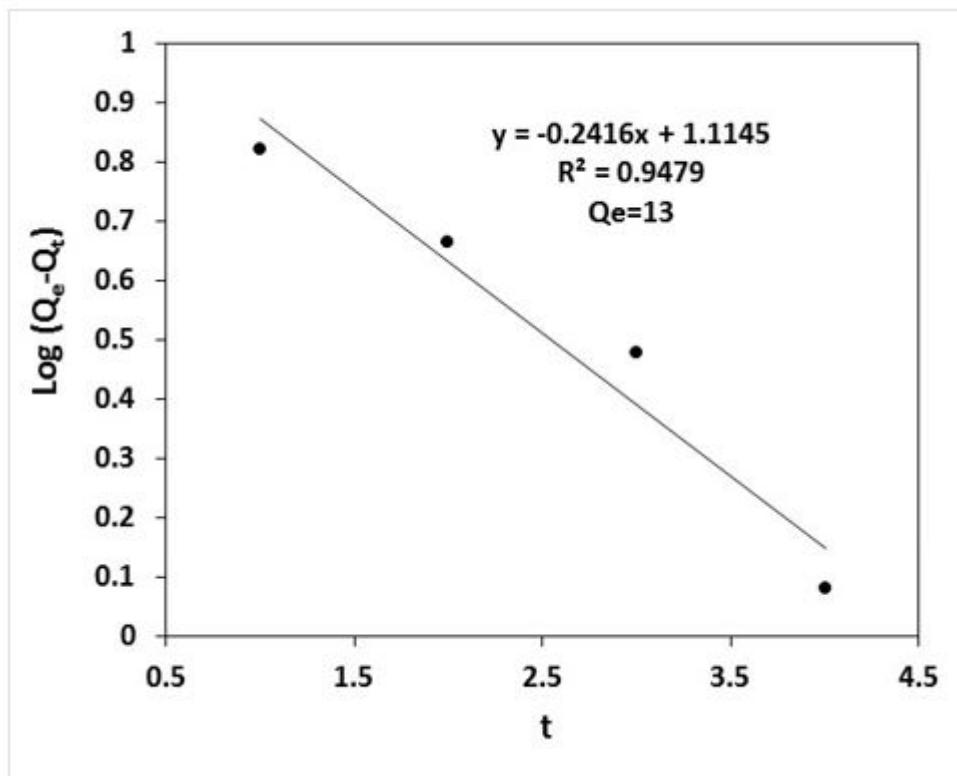


Figure 3: Pseudo-first-order kinetic plots for the adsorption of U (VI) ion at room temperature

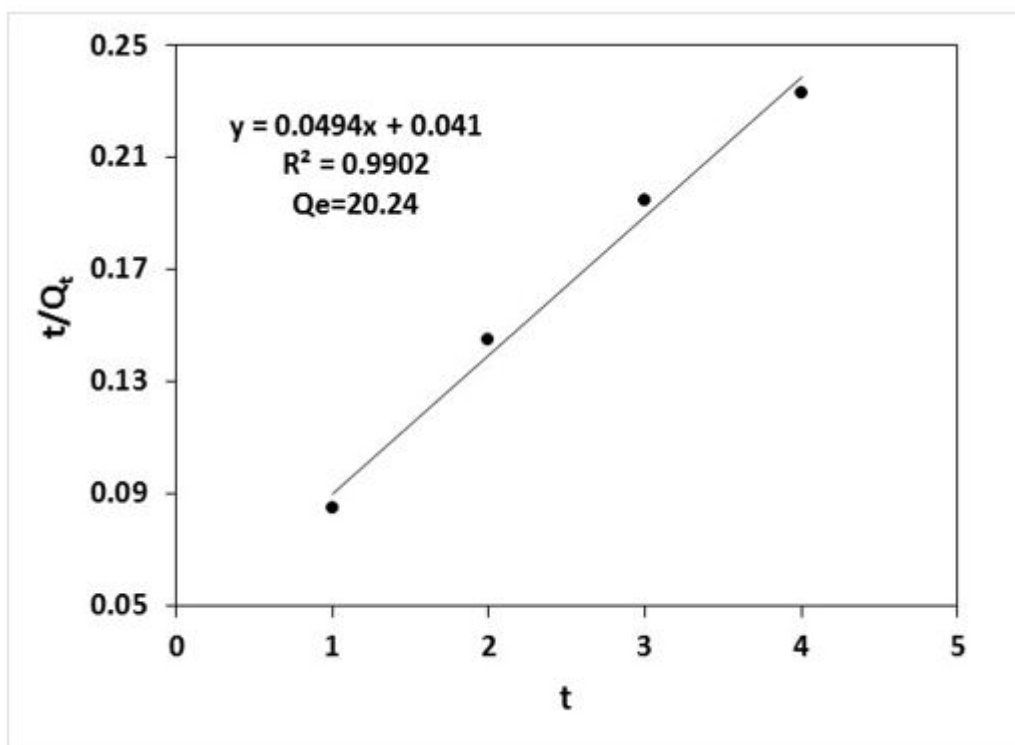


Figure 4: Pseudo-second-order kinetic plots for the adsorption of U (VI) ion at room temperature

Effect of concentration:

In order to recognize that the concentration at which the absorption capacity of our designed absorbent is maximum, changed concentrations of Uranium (VI) solutions (100-1000ppm) were prepared and absorbents were put into them and kept for 5 hours. The absorption capacities at different concentrations were measured using UV-Vis absorption spectroscopy. The plotted graph (Figure 5) shows that, with the increase of Uranium (VI) concentration, the adsorption amount of Uranium (VI) increased, and then at some higher concentration, the adsorption reached a plateau value. Highest adsorption capacity achieved was 166.84 mg/g at 1000 ppm.

The interaction of uranium (VI) ion with the hydrogel were examined by Langmuir isotherm. The assumptions on which the Langmuir isotherm is established on are- monolayer adsorption, identical adsorption sites and any molecule to be adsorbed is independent of its neighboring sites occupancy [22]. Eqⁿ (7) is the equational expression of Langmuir Model.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \dots \dots \dots (7)$$

Where, C_e is the equilibrium concentration (mg/L), Q_m is the monolayer saturation adsorption capacity of the adsorbent (mg/g), Q_e is the equilibrium adsorption capacity and K_L is the Langmuir adsorption constant (L/mg). Here, a plot of C_e/Q_e vs. C_e should be a straight line with a slope ($1/Q_m$) and an intercept will be ($1/Q_m b$). The isotherm data has been interpreted using Langmuir isotherm as shown in Figure 5. The high value of correlation coefficient ($R^2=0.999$) indicates a good compatibility between the parameters and confirms the monolayer adsorption of U (VI) ions onto the hydrogel.

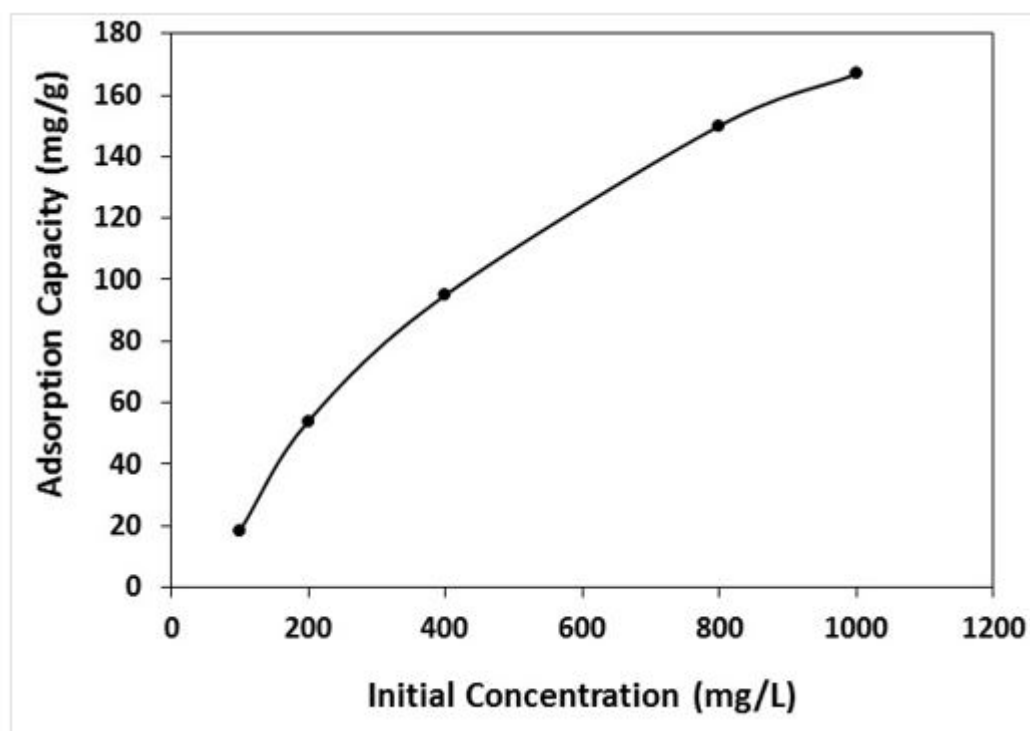


Figure 5: Effect of concentration on the adsorption capacities of starch acrylic acid-acrylamide hydrogen (pH 3.57, contact time 5 h, room temperature)

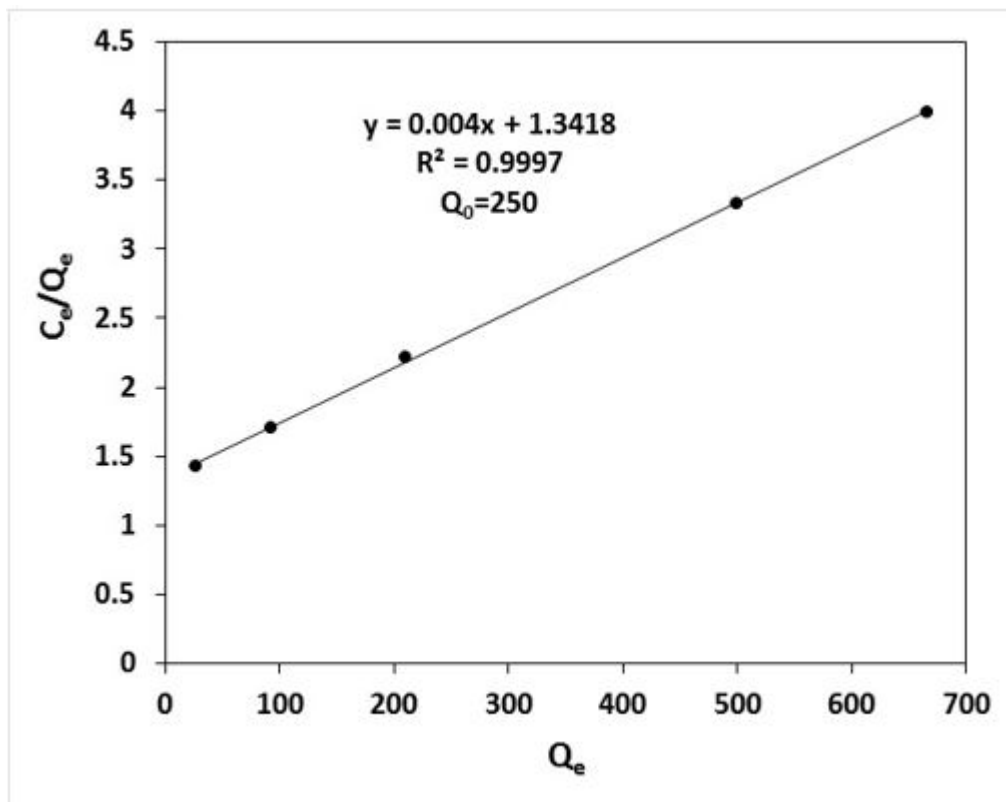


Figure 6: Langmuir isotherm plot for U(VI) adsorption at room temperature

Effect of pH:

To understand the absorption mechanism the pH value of the solution of U (VI) is an important factor. The absorption capacity studied at pH 1.670, 2.475, 3.57, 5.358, 6.188. Figure shows the effect of pH value of Uranium (VI) solution on the absorption capacities of absorbent. From the graph (Figure 7) it is evident that the absorption capacity was highly influenced by pH of the medium. With the increase of pH value some amount of precipitate was formed. As a result absorption capacity decreased. The best adsorption capacity (95 mg/g) was obtained at pH 3.57.

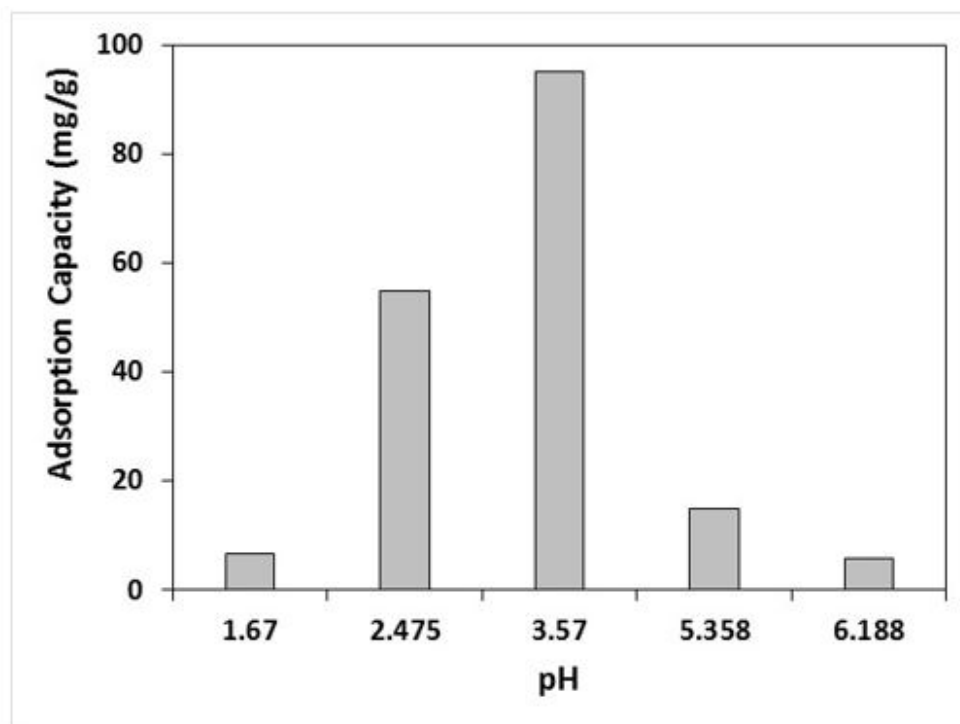


Figure 7: Effect of the pH values on the adsorption capacities of starch AAc -AAM hydrogel for U (VI). (contact time 5 h, concentration 400 ppm, room temperature)

Effect of Temperature

To understand the absorption mechanism the temperature of the solution of U(VI) was varied. The absorption capacity studied at temperature 30°C (room temperature) and 60°C. Figure 8 shows the effect of temperature of U(VI) solution on the absorption capacities of absorbent. From the figure it is evident that the absorption capacity was not greatly influenced by temperature of the medium. With the increase of temperature, absorption capacity slightly increased. The adsorption capacity increased from 92.43 mg/g at 30°C to 99 mg/g at 60°C temperature.

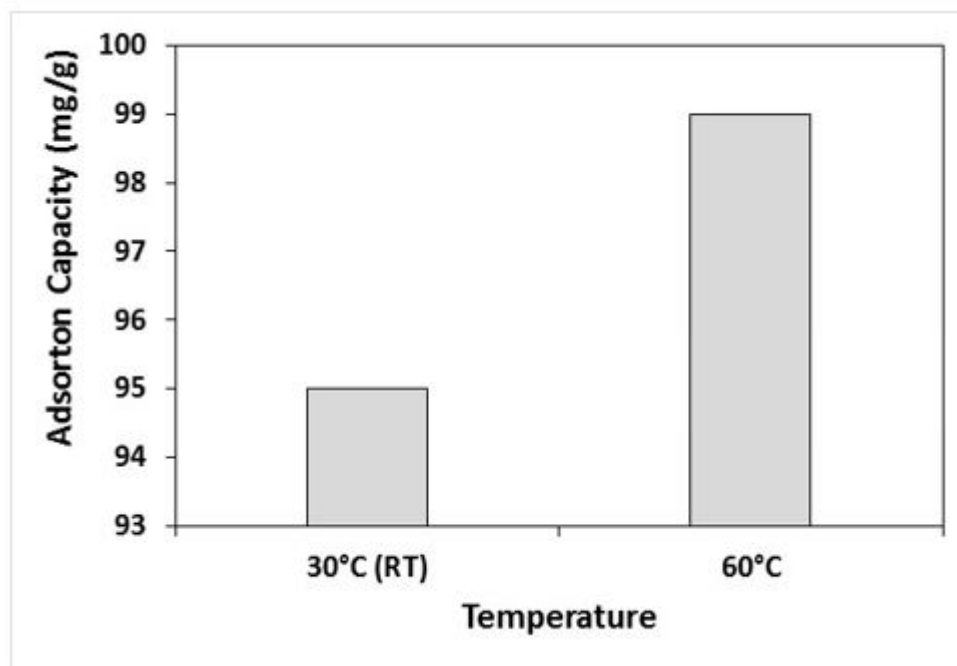


Figure 8: Effect of temperature on adsorption capacities of starch AAC and AAm hydrogel for U(VI) (contact time 5 h, concentration 400 ppm, pH 3.57)

Desorption of Uranium (VI)

The desorption from the absorbent were carried out using 2M HCl for 24 hr. Desorption studies can help elucidating the mechanism of an absorption process. The desorption ratio was 96%.

Reuse

After desorption, desorbed hydrogel reverted back to its previous phase by alkali treatment. After alkali treatment, desorbed hydrogel which was used again to adsorb U(VI). The result indicate that the adsorbent is able to swell and adsorb U(VI) again.

Conclusion

Starch-Acrylic acid-Acrylamide hydrogel were prepared by the application of gamma rays from Co-60 source at room temperature. The prepared absorbent was applied for absorption of Uranium (VI). Absorption capacity of the absorbent was examined through changing contact time, pH, temperature, concentration of Uranium (VI) solution. Absorption of U(VI) reached the highest value of 166.84 mg/g after 5 hours, at pH 3.7 and 1000 ppm U(VI) concentration. The desorption of U(VI) was successfully done and the adsorbent was effectively reused. The results indicate that the starch-acrylic acid-acrylamide hydrogel absorbent can be used for U(VI) removal from contaminated water.

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Competing interests

The authors declare that they have no competing interests

Authors' contributions

Nazia Rahman (Principal Scientific Officer) designed the experiments, analyzed and interpreted the U(VI) adsorption data and also wrote the manuscript.

Shahnaz Sultana (Senior Scientific Officer) performed the experimental part of radiation grafting.

Md. Nabul Sardar (Scientific Officer) performed the experimental part of U(VI) adsorption.

Nirmal Chandra Dafader (Chief Scientific Officer) contributed in writing the manuscript.

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