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Succinate-modified Flax Seed Hydrogel for the Cobalt Remediation from Polluted Water for Public Health Concern

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Abstract: An efficient adsorbent for removing Co (II) ions from polluted water was developed by esterification of mucilage from flax seeds. The esterified flax seed mucilage was neutralized to prepare its sodium salt (Na-FSM). To having good capacity for holding water, it was tested for its potential to remove Co (II) from aqueous solution. The effects of initial concentration of Co (II) ions, the Na-FSM dose, time to contact, temperature, and the pH was investigated through batch adsorption tests. The optimum conditions at which highest Co (II) removal was took place were: concentration of Co (II) ions = 100 mg/L, the Na-FSM dose = 30 mg/g, time to contact = 30 min, temperature = 298K, and the pH= 6. Hence, at these conditions it could be best to established adsorption isotherm and adsorption kinetics.

Keywords: Flax seeds, hydrogel, wastewater treatment, pH, temperature, cobalt

1. Introduction

The persistence, bioaccumulation, and toxicity of heavy metals make them a significant class of environmental contaminants. The planet's ecological equilibrium is seriously threatened by their endurance in ecosystems, which also puts humans and other species that feed them at danger [1]. Cobalt (Co^{2+}) is amongst the many heavy metals that are frequently a cause for worry. For both humans and animals, cobalt (Co) is an active component of vitamin B12, also known as cobalamin. It participates in metabolism, strengthens the immune system, and has antimicrobial properties [2]. Unfortunately, the quantity of Co (II) released into the environment exceeds allowable norms due to both natural and man-made processes, putting the health of living creatures at risk. Exposure to high concentrations of Co (II) can result in diarrhea, vomiting, nausea, low blood pressure, bleeding, thyroid damage, and cardiac problems. Co(II) exposure at low concentrations can result in anemia, anorexia, and persistent edema [3].

Although Co^{2+} is useful in several industrial applications, it is hazardous environmental pollutants that can take many different forms, increasing its bioavailability and related dangers. Agencies like the US EPA and the World Health Organization have swiftly set permitted standards for this metal in drinking water. Co-exposures and increasing environmental concentrations that above both allowable limits are directly linked to anthropogenic activity in the form of waste, industrial manufacture, and industrial discharges.

Heavy metals have been eliminated from polluted water by combining several physicochemical techniques. These include techniques such as osmosis [4], ultrafiltration membrane systems [5], chemical precipitation [6], precipitation [7], and ion-exchange [8]. However, adsorption is the technique that is gaining the most attention because of its several benefits [9].

It is a preferred approach over others due to the high enrichment capacity of adsorbents, straightforward separation procedures, and the use of low-cost, environmentally benign materials as sorbents [10]. Activated carbon, biological materials, and agricultural waste are common components of biosorbents. The comparatively poor sorption capacity of many conventional materials is a major drawback, which is fueling research to create novel, affordable, and eco-friendly sorbents for water treatment [11].

Polysaccharide-based hydrogels have garnered significant attention in recent years. These materials are very promising sorbents for the sequestration of Co^{2+} ions from groundwater leachates and wastewater because they may be chemically functionalized using carboxylic acid anhydrides (such as succinic anhydride) to improve their metal-binding capacity. Due to their inherent stimuli-responsive, super-porous, superabsorbent, and non-toxic qualities, mucilage and polysaccharide-rich materials have been successfully studied for the development of efficient sustained-release drug delivery systems [12-27].

Linum usitatissimum L. (Flax) seeds extruded a hydrogel called Flax seed hydrogel (FSH). FSH has been successfully employed as a sustained-release agent for the encapsulation of the pH-responsive drug delivery systems [28, 29]. The goal of this research is to create a chemically improved, sustainable super-sorbent made from FSH that effectively removes Co^{2+} ions from the aqueous environments. By transforming the FSH into its sodium succinate form (Na-FSH), which increases the availability of active functional groups, the study aims to improve the metal-binding capability of FSH. To ascertain their roles in improving sorption efficiency, the impact of important operational variables likewise initial metal concentration, sorbent dose, contact duration, pH, and temperature will be statistically evaluated.

2. Materials and methods

2.1. Materials

Before doing any more testing, flaxseed that had been gathered from a nearby store was physically cleaned by removing dust and garbage and separating the seeds. The flaxseed was washed before extraction, and all experimental procedures were carried out using deionized water (DI). No additional purification was necessary because all of the reagents and solvents are of analytical purity or above. Before beginning any experiments, all glassware was carefully cleaned with nitric acid.

2.2. Isolation of hydrogel from Linseed and synthesis of sorbent

The hydrogel from flaxseeds (FSH) was isolated according to the procedure reported by [28] and the adsorbent was synthesized according to the procedure reported by [24].

2.3. Sorption studies

Batch adsorption experiments have been used to identify the optimal conditions for the adsorption of Co^{2+} ions removal onto the Na-LSH sorbent as well as the impact of numerous significant critical factors. The initial metal concentration, the amount of sorbent employed, the pH of the solution, the contact duration, and the temperature were the five main factors that were examined. Metal stock solution of 1000 mg/L of Co^{2+} was made by dissolving Cobalt salt in 1 L of DI. The stock solution was diluted to create working solutions at different concentrations, and the pH of each was settled. An Erlenmeyer flask containing 100 mL of a metal ion solution (typically 100 mg/L) was set on a shaking thermostat and shaken for 30 min at a set temperature for each experiment. To separate any remaining Co^{2+} ions in the solution, the solid sorbent was collected via a filter after shaking. The amount of Co^{2+} ions removed from each sorbent material was calculated using the standard formulas listed in Equations 1 and 2, where q_e equals to the amount of Co^{2+} ions adsorbed by each sorbent. The concentration of both ions still present in the filtrate was determined using Flame Atomic Absorption Spectroscopy (FAAS).

$$q_e = \frac{C_i - C_e}{m} \times V \qquad (1)$$

$$Percentage\ uptake = \frac{C_i - C_e}{C_i} \times 100 \qquad (2)$$

The equilibrium sorption capacity is represented by q_e (mg g^{-1}) in these equations, where C_i and C_e represent the starting and final metal concentrations, respectively (mg L^{-1}); V is the solution's volume (L), and m is the adsorbent's mass (g).

2.3.1. Effect of initial metal ion concentration

It was examined how the initial concentration of metal ions affected the sorption efficiency of Na-SRG. For 30 min at 200 rpm at 298 K, the sorbent (30 mg) was mixed with 100 mL of Co^{2+} solutions at different concentrations (20 to 160 mg L^{-1}). The of sorption equilibrium was subsequently determined using the results of these tests. The results of these tests were utilized to determine the ideal beginning metal concentration for further studies.

2.3.2. Effect of sorbent dose

Different masses of Na-LSH, ranging from 20 to 90 mg, were added to 100 mL solutions of 100 mg L^{-1} of Co^{2+} produced from the preceding experiment in order to determine the optimal amount of sorbents. Finding the fewest sorbents required to maximize the adsorption of metal ions from the aqueous solution was the aim of this experiment.

2.3.3. Effect of pH

Using 30 mg of sorbent and 100 mL solutions of Co^{2+} (100 mg L^{-1}), the impact of pH on the adsorption efficiency was evaluated. To find the ideal conditions for metal adsorption, the initial pH of these solutions was changed from 2 to 10 using 1 M HNO_3 or NaOH.

2.3.4. Effect of contact time

Experiments were conducted by swirling an ideal dosage of sorbent (30 mg) in 100 mL of metal solutions at a concentration of 100 mg L^{-1} and pH 6 in order to investigate the sorption kinetics and comprehend the process. At 298 K, the contact time was examined for 5 to 120 min. FAAS was used to assess the residual concentrations of Co^{2+} in the supernatant, and pseudo-first order and pseudo-second order kinetic models were used to analyze the results.

2.3.5. Effect of temperature

We looked at the sorption process's temperature dependency in order to evaluate its thermodynamic character. In accordance with standard protocol, we tested the metal uptake throughout a temperature range of 298 to 348 K to determine if it was endothermic or exothermic and whether it was spontaneous or not.

3. Results and discussions

3.1. Effect of initial metal ion Concentration

The effectiveness of Na-FSH in sorbing Co^{2+} ions by varying their starting concentration. The amount of metal (mg metal per gram of sorbent, or q_e) that Na-FSH could store rose as metal ionic concentrations increased until the quantity of accessible metal ions approached saturation, as seen in Figure 1. At the starting condition of 100 mg L^{-1}, Co^{2+} was most efficiently sorbed; rising concentrations of either ion did not provide Na-FSH any further sorption capacity. This suggests that more research is needed to assess the sorption effectiveness of Na-FSH at greater starting metal ionic concentration levels. The increase in accessible metal ions and the resulting larger concentration gradient that would propel the transfer of metal ions to Na-FSH were once thought to be the causes of the increased sorption capacity. The plateau at initial values over 100 mg L^{-1} shows that Co^{2+} ions filled the anion-exchangeable sites on the surface of Na-FSH, preventing further cation sorption [30, 31].

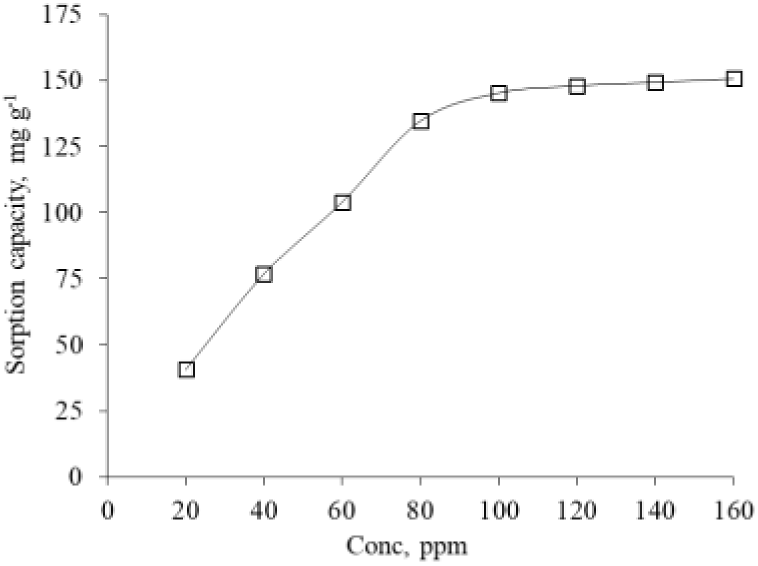

Figure 1: Effect of Co^{2+} ions concentration.

3.2. Effect of sorbent dosage

The ideal amount of sorbent required to achieve the highest removal of metals was determined through experimental testing. The results showed that the adsorption of both Co^{2+}

with increasing dosages or masses of Na-FSH was enhanced due to the increased number of available binding sites from the greater quantity of sorbent introduced into the system. However, the rate of metal uptake decreased slightly once a correct mass of 30 mg was reached. The total concentration of the metal ions in the solution determines this drop; any extra mass of sorbent beyond the 30 mg threshold has vacant binding sites due to insufficient metal ion concentration in the solution [27, 32]. Based on this data, it was concluded that 30 mg of Na-FSH would be the ideal mass of sorbent to be utilized for further experiments, as shown in Figure 2.

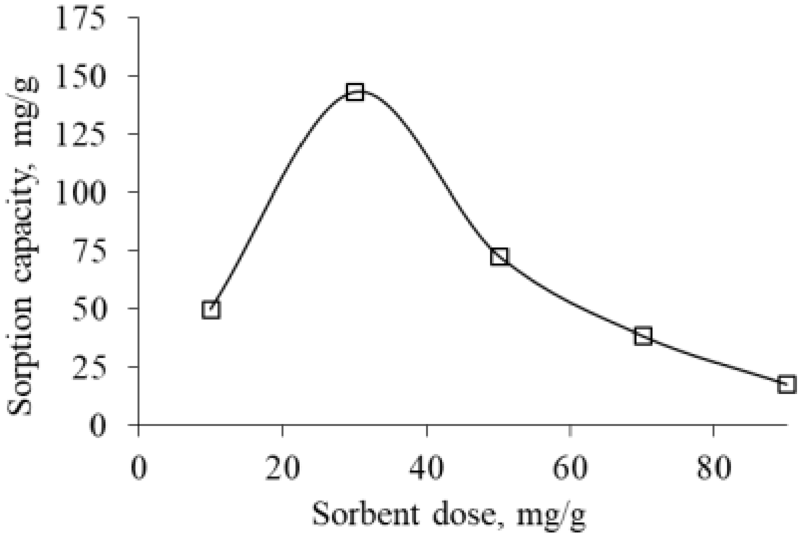

Figure 2: Effect of Na-FSH dose.

3.3. Effect of pH

Because pH regulates surface charge and the ionization state of functional groups, it has a significant impact on the sorption capacity of Na-FSH. Na-FSH materials with a pH range of 2.0–10.0 were used for Co^{2+} sorption experiments (Figure 3). The protonation and conversion of Na-FSH into its acid form (S-FSH) is thought to be the source of the low adsorption values seen in acidic media. This created situation prevents metals from being absorbed by vault-like cation exchange sites. Na-FSH sorption capacity rose with pH, reaching its maximum at pH 6.0. The fast growth of metal sorption at this increased range is facilitated by the deprotonation of different functional groups and the establishment of a negative charge when solution pH exceeds the sorbent's point of zero charge (pH_{ZPC}). Beyond this zone, the precipitation of $Co(OH)_2$ lowers the total concentrations of metal ions available in solution, reducing exchange reaction efficiency [35]. The region surrounding the pH_{ZPC} exhibits a positive charge, indicating a limited capacity to bind with metal ions. The ideal pH for carrying out the remaining sorption experiments was thus found to be 6

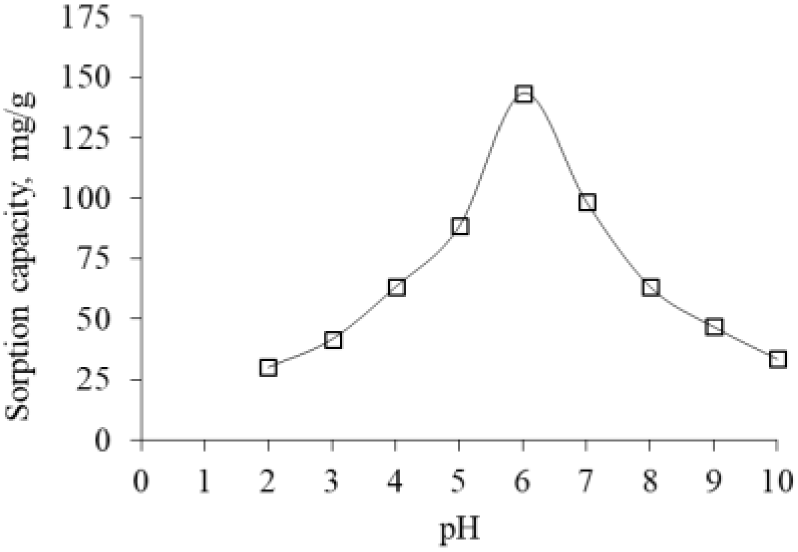

Figure 3: Effect of pH.

3.4. Effect of contact time

Total sorption capacity is significantly impacted by the length of time that the sorbent's active sites are in contact with the metal ions in solution. Evaluation of contact duration helps in identify the kinetic model most appropriate for the material and sheds light on the adsorption mechanism. For Na-FSH, contact time across both Co^{2+} ions was calculated. The majority of the metals were adsorbed after 30 min of contact, which produced an 85% elimination of metal ions (Figure 4). An abundance of sodium-succinate functional groups on Na-FSH and the quick kinetics of the ion-exchange mechanism, which exchanges Na^+ ions with Co^{2+} ions, were the causes of this initial fast metal absorption. After 30 min, the rate of metal adsorption drastically decreased because the arriving cations' repulsion with the metal ions that had previously been adsorbed limited access to vacant active sites for further sorption. No appreciable increases in metal ions adsorbed were seen after 30 min, suggesting that lengthening the contact duration will not boost Na-FSH's sorption capability [23, 36]. This demonstrates that Na-FSH will soon reach equilibrium, making it a useful and advantageous substance.

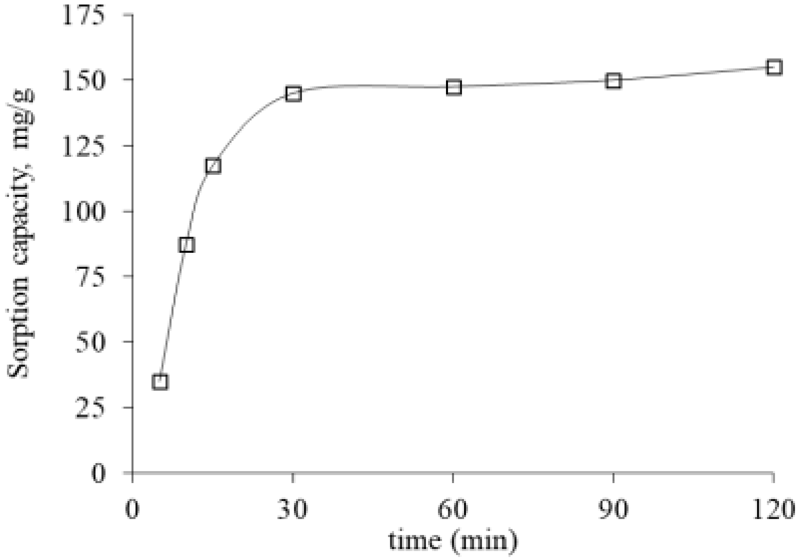

Figure 4: Effect of time.

3.5. Effect of temperature

In order to learn more about the thermodynamics of the sorption process more particularly, whether it is exothermic or endothermic, the impact of temperature on the performance of Na-FSH for the sorption of hazardous metals has been examined in this work. The temperature range at which the experiments were carried out was 298 K to 343 K. The sorption process is exothermic because, as Figure 5 illustrates, the sorption capacity of the adsorbent was greatest at the lowest temperature and reduced as temperatures rose. When the temperature is lower than 298 K, the mobility of Co^{2+} ions would not be able to occupy all of the active sites on the sorbent's surface due to the higher temperature at which Na^+ ions in the sorbent moved quickly. The amount of metal cations that can be absorbed into the sorbent would decrease as the temperature rises due to the increasing activity of Na^+ ions [23, 24]. These findings suggest that 298 K is the ideal temperature for the sorbent to absorb Co^{2+} ions.

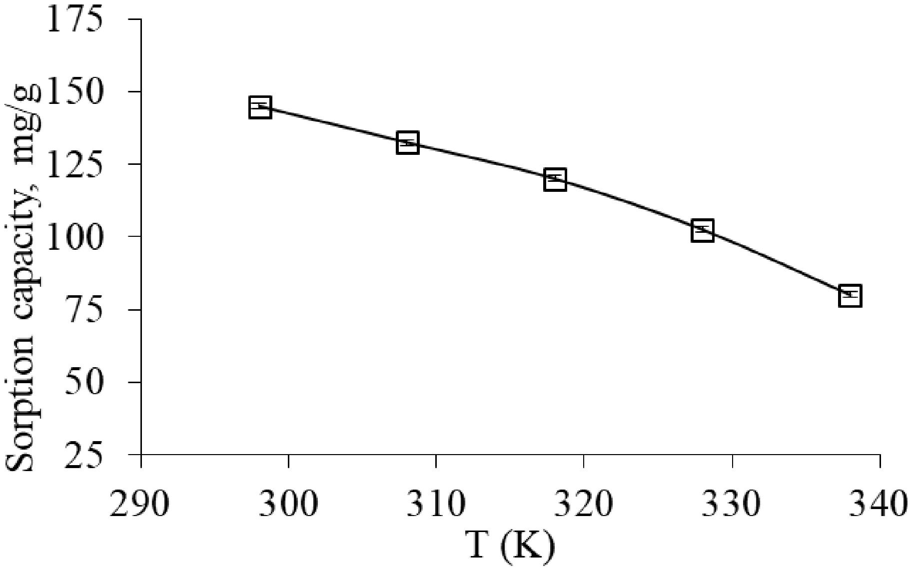

Figure 5: Effect of temperature.

4. Conclusions

Through an esterification process, this study effectively produced a novel biosorbent, the sodium salt of succinylated flax seed hydrogel (Na-FSH). Numerous operating factors had a considerable impact on how well Na-FSH absorbed Co^{2+} ions from aqueous solutions. Over 85% of both metals were absorbed in the first half hour of the operation due to the fast sorption kinetics. Na-FSH is a very effective, reusable, and super-sorbent with very promising potential for the selective absorption of Co^{2+} from polluted water, as confirmed by the measured high sorption capacities and favorable kinetics.

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