SYNTHESIS OF *Scylla Serrata* SHELL DERIVED CHITOSAN-COATED MESOPOROUS MAGNETIC NANO ADSORBENT FOR Cr(VI) REMOVAL FROM AQUEOUS SOLUTIONS

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ABSTRACT

Mesoporous magnetic chitosan nano-sorbents (m-MCNS) were synthesized by the co-precipitation reaction of *Scylla serrata* shell-derived chitosan and iron oxide nanoparticles using glutaraldehyde cross-linkers. The prepared m-MCNS were highly crystalline, porous, and spherical with an average size of 21.6 nm and surface area of 28.3 m²/g and exhibiting magnetic saturation of 9.1917 emu/g. The synthesized m-MCNS was tested to determine its adsorptive capacity Cr (VI). An optimized removal of 98.7% was obtained with 0.3 gram of m-MCNS at pH of 5.5 at 303K for an initial concentration 100 mg/L of Cr(VI). Langmuir isotherm fit experimental data better than other models. The adsorptive kinetics agreed well with the pseudo-second-order model. The m-MCNS adsorbent has greater potential to remove Cr (VI) from the wastewater.

Keywords: Nano-sorbents, Adsorption, Kinetics, Isotherm, Chitosan, Mesoporous

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INTRODUCTION

The environment, human health, and aquatic life were seriously affected by the industrial exit which contains poisonous substantial metal toxins. Among all these, after Arsenic the Chromium is one of the important and essential heavy metals used in the various sectors which tends to severe threat when it is mixed with water sources and more toxic. Cr³⁺ and Cr⁶⁺ are the significant oxidation types of chromium that exists in wastewater releases.¹ Among these, the Cr (VI) is considered as a harmful metal and makes cancer-causing and poisonous impacts people and displays amphibian life poisonous.² Even though the wide assortment of Cr (VI) expulsion strategies, the adsorption is increasingly fit given its selectivity, ease, profoundly effectiveness, simple dealing with, re-usability, and suitability.³ In recent years, the synthesis of magnetic adsorbents was proved to be more prominent for the exclusion of Cr(VI) by simplifying the practice in recuperating the adsorbed material with an external magnet when compared to coagulation and precipitation.⁴ Chitosan is a natural biopolymer available in large quantities in the form of chitin and derived from the shells of shrimp, crab, prawn, and crawfish.⁵ The cross-linking of Chitosan remarkably improved in the previous research studies for targeted drug delivery, dye removal, heavy metal removal, and protein adsorption with the prolonged ability with higher crystallinity, hydrophilicity, degradation.⁶ In this exploration, the glutaraldehyde crosslinked chitosan which has been separated from *Scylla serrata* shell, deacetylated and was adequately covered on the magnetic iron oxide by ultrasonic bath tailored co-precipitation strategy. The physio-chemical, morphological, surface, porosity, functional bonds, and magnetic properties were characterized. A lot of sorption tests were conducted to analyse the optimal operating conditions.

EXPERIMENTAL

Materials and Methods

All the reagents and chemicals were procured from Sigma-Aldrich, Chennai, India. All the analytical reagents were made with the use of de-ionized water.⁷

Extraction of Chitosan from Crab Shell

The crab shells were collected from the local market in Chennai, India and washed to remove impurities. The dried shells were ground into a fine powder and stored at 4°C. In the demineralization process, 2M of

HCl was added to the powdered shell at 60°C and the mixture was agitated at 200 rpm for 2 hr.⁸ The resultant shells were deproteinized by adding it with 3M of NaOH at 80°C with the agitation rate of 200 rpm for 2 h. The organic compounds present in the mixture were treated with a solution that contains an 8:2 weight ratio of 0.1M H₂O₂ and 10M HCl. The mixture was washed several times with acetone and dried for 2 hr at 30°C to obtain chitin. The deacetylation of the chitin was carried out by treating it with 15M of NaOH at 110°C under vacuum with constant stirring for 5 h and filtered.⁹ The resultant chitosan was cooled and rinsed thoroughly with de-ionized water until the solution pH approached neutral. The chitosan was then allowed to dry overnight.

Synthesis of m-MCNS Magnetic Nanoadsorbent

The m-MCNS were prepared by co-precipitation reaction¹⁰ aided with ultrasonic bath. FeCl₃ and FeSO₄·7H₂O were taken with 2:1 by weight in 50 ml of H₂O at 40°C for 1 hr at a 200rpm agitation rate. 0.35 g of extracted chitosan was added with 15 ml of glutaraldehyde cross-linking agent and thoroughly stirred for 2 hr at 200 rpm. The co-precipitation reaction was initiated by adding a 50 ml drop-wise solution of NH₄OH with the reaction mixture which abandoned reddish-brown colored into black. The slurry containing magnetic chitosan particles was several times washed with water and ethanol and dried in an oven at 60°C. The m-MCNS were characterized by XRD, FT-IR, VSM, FESEM and BET.

Adsorption Studies

1,000 mg/L of Cr (VI) was prepared by dissolving 2.857 g of K₂Cr₂O₇ in 1000mL of H₂O and kept as a stock solution.¹¹

$$\%Removal = \frac{(C_i - C_o)}{C_i} \times 100 \quad (1)$$

Where, C_i is the initial Cr (VI) concentration, C_o and C_t are the initial and final Cr (VI) concentration (mg/L) were analyzed by AAS spectrometer.

Adsorption Isotherms

The batch adsorption data were examined for the equilibrium characteristics.

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$Q_e = K_F C_e^{1/n} \quad (4)$$

$$Q_e = B \ln(K_T C_e) \quad (5)$$

Where, Q_e and Q_m are the equilibrium and highest monolayer adsorption capacity of m-MCNS (mg/g), K_L , K_F , K_T is the Langmuir, Freundlich and Temkin constant respectively.

Chemical Kinetics

The separation time can be computed through kinetics studies using the following equations:¹²

$$\text{Log}(Q_e - Q_t) = \text{Log}Q_e - 0.4342k_1t \quad (6)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (7)$$

Where Q_t is the adsorption capacity of m-MCNS at time t (mg/g), and k_1 and k_2 are kinetic constants.

RESULTS AND DISCUSSION

Characterization of Adsorbent

The XRD pattern of m-MCNS (Fig.-1a) showed the characteristic peaks of 30.36°, 35.72°, 43.48°, 53.83°, 57.39°, and 62.12° corresponding to planes corresponding to the existence of the Fe₃O₄ nanoparticles. It also shows the absence of the peak at 33.15° for FeO(OH) and 21.22° for Fe₂O₃ confirmed that the prepared m-MCNS were free from iron-containing impurities. Fig.-1b illustrates the

SEM micrograph image of m-MCNS which proves the spherically shaped nanoparticles with ample void spaces were observed.

Fig.-1:(a) XRD and (b) SEM Image of m-MCNS Particles

The IR absorption peaks (Fig.-2a) at $3,780\text{ cm}^{-1}$, $3,711\text{ cm}^{-1}$ and $3,645\text{ cm}^{-1}$ indicate the presence of intermolecular hydrogen-bonded N-H stretching. Also, the peaks at $2,883\text{ cm}^{-1}$, $2,341.35\text{ cm}^{-1}$, $1,597.60\text{ cm}^{-1}$, 640.07 cm^{-1} , and 573.54 cm^{-1} correspond to the bending vibrations of -CH, stretching vibrations in -CH₂, presence of -NH₂ from glucosamine functional residue, and Fe-O vibration on the surface of Fe₃O₄, respectively.¹³ VSM analysis examined the magnetic characteristic of the prepared nano-sorbent by oppressing it in the external magnetic field. The VSM hysteresis produced a magnetization value of 9.1917 emu/g ¹⁴ (Fig.-2b). Results of the BET analysis of the m-MCNS particles showed a surface area of $28.29\text{ m}^2/\text{g}$, pore volume of $0.098123\text{ cm}^3/\text{g}$.

Fig.-2:(a) FTIR Spectrum (b) VSM Hysteresis Curve of m-MCNS Particles

Influence of Operating Parameters

Figure-3a, revealed that with the increment of m-MCNS dosage the % Cr(VI) exclusion was increased and then decreased from 0.3 to 0.6 g. It is because of the sufficient adsorption sites provided by the nano-adsorbent at higher dosages. From Fig.-3(b), it was noted higher removal was attained within 10 min. and the gradual increase of the removal was observed from 10 to 50 min at the agitation rate of 200 rpm. It is because of the more surface area of contact and the mesoporous nanostructure provided by m-MCNS adsorbent. Fig.-3(c), shows that the removal increments with increasing the pH from 3 to 5.5. It is because of the acidic condition inducing the electrostatic interaction between the negative $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- ions to the positively charged protonated $-\text{NH}_3^+$ groups present on the porous surfaces.¹⁵ At the lower pH values, the Cr(VI) removal was increased because of the presence of more amino groups in the adsorbent which enables and favors in conducting the desorption experiments¹⁶. Figure-3(d) shows the % Cr (VI)

removal was increased by escalating the concentration from 10 to 100 mg/L, more. It was due to the higher functional groups present in the highly porous structure. It was observed that 98.7% Cr(VI) exclusion was obtained at the optimal conditions such as 100 mg/L, 0.3 g of m-MCNS dosage, acidic pH value of 5.5, and at the contact time of 60 min.

Fig.-3: Influence of Operating Parameters on Cr(VI) Exclusion (a) dosage (b) Time (c) pH (d) Initial Concentration

Equilibrium Adsorption Studies and Kinetics

The statistics of Cr(VI) removal by m-MCNS adsorbent fit the Langmuir adsorption isotherm model better (with Q_m (mg/g) value of 98.04, and K_L (L/mg) value of 0.214) which implies that it follows monolayer chemisorptions (Fig.-4a). The pseudo-second-order kinetics in aligned with the experimental values. The experimental adsorption limit of 24.33 mg/g is validated with the trial estimation of 25.73 mg/g (Fig.-4b).

Fig.-4:(a) Comparison of Isotherms and (b) Kinetics for the Cr (VI) Removal by m-MCNS

CONCLUSION

The batch adsorption experiments were modelled, and the operating conditions were optimized. 98.7 % of maximum Cr (VI) removal efficiency was obtained with the optimal conditions at an adsorbent dosage of 0.3g, contact time of 60 min, initial Cr (VI) concentration of 100 mg/L, and at a pH of 5.5. It has been concluded that the m-MCNS magnetic nano adsorbent is considered as a promising potential adsorbent for Cr (VI) removal from its aqueous mixture.

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