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Chitosan crosslinking into magnetic multi-walled carbon nanotubes beads for efficient Cr(VI) removal

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Heavy Metals Adsorption

Conventional adsorbents

Nano-adsorbents

Less active sites
Lack of selectivity
Low adsorption kinetics

Standard

Highly efficient

- High surface areas to volume ratios
- Smaller pores with high permeability
- High mechanical & tensile strengths
- High electric & thermal conductivity
- Energy saving & low cost
- High adsorption capacity
- Associated sorption sites
- Short intraparticle diffusion
- Tunable pore size & surface chemistry

Carbon Nanotubes

As grown CNTs

Inner pores blocked

Heat treated $\sim 350^\circ\text{C}$

Amorphous carbon removed,
metal catalyst oxidized,
adsorption increased

Acid treatment

Catalyst removed, adsorption
increased

Functionalized

New functional groups added
For nonpolar/planer chemical:
adsorption decreases and for
polar chemical: adsorption
increased

Non-covalent
functionalization

Wrapping the polymers as
additional functional groups
such as chitin/chitosan can
further increases the
adsorption

- Catalyst
- Oxidized catalyst
- Amorphous carbon

Pan and Xing, B. (2008). *Environ. Sci. Technol.* 42, 9005-9013.
Gatabi et al. (2016). *J. Molecul. Liq.* 216, 117-125.

Chitosan

- Chitosan is an excellent bio-adsorbent due to high hydrophilicity, amine and hydroxyl groups.
- It has been applied in the treatment of organic pollutants, including HMs in aqueous environmental system.
- Previously demonstrated that the adsorption capacity of CNTs can be further enhance via modifications with chitosan.

Gatabi et al. (2016). *J. Molecul. Liq.* 216, 117-125.
Huang, et al. (2018). *Chem. Eng. J.* 339, 259-267.

Encapsulation

- Alginate has been utilized for the encapsulation of chemical and biological compounds due to its nontoxicity, high biocompatibility, and especially, the ability to form crosslinks with cations for the material stabilization
- Surface functional groups of alginate are able to capture metallic ions via ion exchange

Vu et al. (2016). *Chem. Eng. J.* 307.

Wang et al. (2018). *Crit. Rev. Environ. Sci. Technol.* 1-39.

Wang et al. (2016). *J. Hazard. Mater.* 308, 75-83.

Objectives

- Developing CS/MWCNTs/Fe beads to enhance adsorptive performance for eliminating Cr(VI) from water.
- Verifying the synergistic effects between CNTs with functionalized surface and CS with rich amine groups, aided by iron particles for magnetism and facilitation of electron transfer.
 - Investigating the effects of parameters i.e. adsorbent dosage, contact time, reaction temperature, solution pH, initial concentration of metals ions.
 - Determining adsorption isotherm, kinetics and thermodynamics characteristics.
- Development of a suitable regeneration scheme to make cost-effective sorbent, and determination of the potential of reusability of CS/MWCNTs/Fe beads for consecutive treatment cycles.

Material Synthesis

CS/MWCNTs/Fe beads

Materials Characterization

- **Morphological study**
 - FE-SEM (JEOL JSM 700)
 - Energy Dispersive Spectrometry
- **Surface chemical analysis**
 - Fourier-transform infrared spectroscopy (FTIR) IR (JASCO FT/IR-460 Plus)
- **Crystallinity analysis**
 - X-ray diffractometry (XRD) (PHILIPS X'PERT Pro MPD)
- **Thermal stability analysis**
 - Thermogravimetric analyzer (TGA)

Experimental Design

Batch adsorption experiments

- Operating parameters such as adsorbent dosage, contact time, adsorbate concentrations, temperature and pH were evaluated
- Cr(VI) by UV-vis spectrophotometer
- Total chromium was measured by ICP-MS
- Optimization studies were conducted by varying the contents of MWCNTs, magnetic particles, chitosan and sodium alginate
- Different adsorption isotherms and kinetic models were applied to fit the experimental data
- Thermodynamic studies were conducted at varying temperature

Morphology (FE-SEM)

Chemical Analyses

Elemental Composition (EDS)

Element	Weight%	Atomic%
C	35.36	46.23
O	48.27	47.39
Na	0.86	0.59
Cl	4.48	1.98
Ca	6.37	2.50
Fe	4.66	1.31

FTIR spectrum

- (a) Oxidized-MWCNTs
- (b) MWCNTs/Fe
- (c) MWCNTs/Fe beads
- (d) CS/MWCNTs/Fe beads

Characterizations

XRD analysis

TGA

Effect of pH on Cr(VI) Adsorption

Point zero charge

Effect of pH

Initial Cr(VI) concentration: 10 mg/L;
Temperature 298K

Cr(IV) Adsorption on CS/MWCNTs/Fe

Effect of adsorbent dosage

Reduction of Cr(VI) to Cr(III)

Initial Cr(VI) concentration: (a) 10 mg/L, (b) 20 mg/L; Adsorbent dosage: 0.5 mg/L;
Temperature 298K, pH: 4.0 ± 0.2

Cr(IV) Removal with Different Adsorbents

Initial Cr(VI) concentration: 10 mg/L; Adsorbent dosage: 0.5 mg/L; Temperature 298K, pH: 4.0±0.2

Effect of Material Composition

Influence of different contents of CS

Influence of different contents of SA

Initial Cr(VI) concentration: 10 mg/L; Adsorbent dosage: 0.5 mg/L; Temperature 298K, pH: 4.0±0.2

Cr(IV) Adsorptivity on CS/MWCNTs/Fe

Effect of initial concentration

Effect of temperature

Adsorbent dosage: 0.5 mg/L; Temperature 298K, pH: 4.0±0.2

Isotherms Study

Isotherm	Parameters	Values
Langmuir	(L/mg)	0.687
	(mg/g)	11.89
	b (L/mg)	0.0841
		0.343-0.032
	R ²	0.975
Freundlich	1/n	0.142
	K _F (mg/L)	7.101
	R ²	0.971

Initial Cr(VI) concentration: 50 mg/L; Adsorbent dosage: 0.5 mg/L; Temperature 298K, pH: 4.0±0.2

Kinetic study

Pseudo 2nd-order: **(a)** initial concentration, **(b)** initial concentration (intra-particle diffusion), **(c)** contents of CS, **(d)** contents of SA, **(e)** temperature, **(f)** pH

Stability/Recyclability

Initial Cr(VI) concentration: 10 mg/L; Adsorbent dosage: 0.5 mg/L; Temperature 298K, pH: 4.0±0.2

Summary

- A composite adsorption material consisting of MWCNTs, chitosan, iron particles, all encapsulated as alginate beads, were successfully synthesized.
- The composite beads demonstrated a high Cr(VI) removal performance with an optimized chitosan and alginate contents. The adsorption kinetics followed closely with pseudo second order model, with a Langmuir maximum adsorption capacity of 11.74 mg/g.
- The observation of Cr(III) validated the hypothesis that the addition of iron particles were capable of facilitating electron transfer from Cr(VI).
- The beads showed up to 76% of Cr(VI) removal efficiency after five cycles of adsorption

Thank you!

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