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The Preparation of Montmorillonite/Carrageenan-Composite Hydrogel for Chromium (VI) Removal from Aqueous Solution

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Abstract: In this study, Montmorillonite/Carrageenan (MMT/CG)-composite hydrogel was synthesized for removal of Chromium (VI) from aqueous solution. The chemical structure, morphological property and thermal decomposition of (MMT/CG)-composite hydrogel has been evaluated by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope Spectroscopy (SEM) and thermogravimetric analysis (TGA), respectively. The X-ray data of (MMT/CG)-composite hydrogel was researched crystallite properties. The results of (MMT/CG)-composite hydrogel CG, and MMT powders had compared each other to research the efficiency of MMT. The efficiency of adsorption parameters (contact time, initial feed concentration, and pH) on Chromium (VI) ion adsorbing capacity of (MMT/CG)-composite hydrogel was also investigated by UV–vis diffusive reflectance spectra. The adsorption capacity enhanced with the adding of MMT in hydrogel. The adsorption process was determined by the Langmuir isotherm model. According to the findings, the MMT/CG-composite hydrogel can be utilized as a suitable adsorbent to removal of Chromium (VI) from aqueous solution.

Keywords: Montmorillonite, Carrageenan, Hydrogel, Adsorption, chromium (VI)

Introduction

Water pollution is increasing day by day following the rapid industrial improvement. Industrial wastes, pesticides, detergents, agricultural fertilizers, dyestuffs, and heavy metals are major pollutions. Heavy metals must be effectively removed from water sources due to their toxic and carcinogenic properties.

Ion exchange, chemical precipitation, chemical oxidation/reduction, reverse osmosis, and ultrafiltration methods are frequently used to remove heavy metal ions. However, these methods have low efficiency and high cost, and they cause significant waste problem. Adsorption is another alternative method (Islam, Angove, & Morton, 2019). It is the accumulation of a substance on the surface of the second phase by passing from one phase to the other, or the retention of adsorbent molecules dissolved in the liquid phase on a solid adsorbent surface or the adhesion phenomenon that occurs at the phase interface because of the concentration change at the boundary surface. It occurs between solid-liquid or solid-gas phases. It has advantages such as low cost, simplicity of design, low energy requirement, high efficiency, ease of use, and reuse of adsorbents. The adsorption method becomes more prominent when environmentally friendly, non-toxic, cheap, and safe adsorbents are used. (Dakiky et al., 2002). In recent years, there has been a lot of research for alternative low-cost materials that are effective and biodegradable, such as hydrogels, agricultural wastes, and clays.

Hydrogels are inexpensive polymeric materials which include hydrophilic groups (such as -COOH, -SO_3H, -OH, -NH_2, -CONH, -$CONH_2$, etc.). They can easily swell in water due to their hydrophilic groups. They are extremely used in heavy metal removal systems because of their high-water holding capacity, biocompatibility, and biodegradability (Ahmed, 2015). Several natural polymers such as gelatin, carboxymethyl cellulose, pectin, chitosan, alginate, carrageenan etc. are utilized for formation of hydrogels.

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Carrageenan is obtained from *Rhodophyceae class* seaweed by some extraction methods from red algae species. It is a linear polysaccharide produced from the most common red algae *Chondrus Crispus* and *Gigartina Mamillosa*. It consists of large and highly elastic molecules in a coiled helical structure. Its flexible structures enable to generate gel forms at room temperature. (Sharma et al., 2022). Thanks to these properties, it is used as a thickener and stabilizer in the food industry and other industrial fields.

Clays are good adsorbent for heavy metal ions, polymer nanocomposites, catalyst, photochemical reactions, and biosensors. They have high chemical and mechanical stabilities and several surface and structure properties. Montmorillonite (MMT) is the commonly preferred clay for industrial utilization. MMT is an alteration forming of volcanic tuff and ash, product of bentonite beds, and of wall rock and pegmatite dikes bordering hydrothermal mineral deposits. It is non-toxic and low-cost, but its adsorption capability is limited by its poor water permeability. To overcome this limitation, MMT can be blended with other materials such as CMC, PVA, PMMA etc. to generate composite hydrogels (Ianchis et al., 2020; Kaşgöz, & Durmus, 2008). These composites have high water permeability, and they are used as adsorbents for heavy metal removal. However, the use of MMT/Carrageenan-composite hydrogels as adsorbent for heavy metal removal has not been studied. In this research, MMT/Carrageenan-composite hydrogels were prepared for *Cr(VI)* ions removal. The adsorption capacity of *Cr(VI)* ions by changing the MMT/CG mass ratio, pH of *Cr(VI)* solution, initial *Cr(VI)* concentration and contact time were investigated. To describe the adsorption character, adsorption isotherm model was examined.

Materials and Methods

Sodium-MMT with a zeta potential of -39.3 mV and a cationic exchange capacity of 71 mequiv/100 g was purchased from Southern Clay (USA) was supplied by Ciba Specialty Chemicals (Thailand). CG and Glutaraldehyde were supplied by Sigma Aldrich.

Preparation of MMT/Carrageenan-Composite Hydrogels

The MMT/CG suspensions were prepared by adding MMT (0.1, 0.2 and 0.3 w/v) to the 1% (w/v) CG solution under vigorous dispersion for 1 hr. 100 ml of MMT/CG suspension was added dropwise to 0.2% (w/v) glutaraldehyde solution using a peristaltic pump for the MMT/CG ratios of 0.1:1, 0.2:1 and 0.3:1 respectively. After the stirring for 1 h, the solidified MMT/CG-composite hydrogels were obtained, they washed with distilled water several times and then dried at 60°C for 24 h.

Characterization of MMT/CG Hydrogels

The MMT, Carrageenan and MMT/Carrageenan composite hydrogels were performed by Fourier transform infrared (FTIR) spectrophotometry (FT-IR Shimadzu IR-Prestige 2) using KBr. The measurement was scanned between 400 and 4000 cm^{-1}. The crystallinity of the samples was performed by wide-angle X-ray diffraction (XRD; Diffractometer Bruker D8 Advance). The X-ray diffractometer was done at 40 kV and 50 mA, with Cu-Kα radiation source (λ=1.54060 Å). The morphology of the composite hydrogels was visualized by scanning electron microscopy (SEM; model Quanta 250, FEI). Thermal analysis of the composite hydrogels were determined by thermogravimetric analysis (TGA; TG/DTA 7300 Hitachi) under nitrogen gas flow from 30°C to 800°C at a heating rate of 10°C/min.

Adsorption Studies

The influence of contact time, pH, and initial concentration of *Cr(VI)* solution on adsorption was investigated. The adsorption was performed on a shaker (120 rpm) at 25^{o}C using 0.2 g MMT/CG composite hydrogels (MMT/CG mass ratio 0.1:1.0 and 0.3:1.0), and 50 mL of Cr (VI) solution (80 mg/L) in a 125-mL conical flask. The *Cr(VI)* solution was collected at certain time intervals and the residual *Cr(V*I) concentration was measured using a UV-vis spectrophotometer (Shimadzu-18A UV-Visible spectrophotometer) at 540 nm (Alemayehu, Singh, & Tessema, 2012).

The amount of adsorbed *Cr(VI)* concentration at time *t* was determined from Equation 1:

$$Qt = \frac{(Co-Ct)\,V}{W} \quad (1)$$

Qt is amount of adsorbed *Cr(VI)* per amount of hydrogel at time t (mg/g), C_0 is initial *Cr(VI)* concentration (mg/L), C_t is *Cr(VI)* concentration at time t (*mg/L*), *W* is weight of dried composite hydrogels (*g*) and *V* is volume of *Cr(VI)* solution (L).

The equilibrium adsorption capacity (Q_e) of the composite hydrogels was determined from Equation 2:

$$Qe = \frac{(Co-Ce)\,V}{W} \quad (2)$$

where C_0 and C_e are initial concentration and equilibrium concentration of *Cr(VI)* in solution (*mg/L*) respectively, *V* is volume of *Cr(VI)* solution (*L*) and *W* is weight of dried composite hydrogels (*g*).

Results and Discussion

FTIR

The FTIR spectra of the MMT powder, CG powder and MMT/CG hydrogel (with MMT/CG mass ratio of 0.3:1 as representative sample) are given in Figure 1. The characteristic peaks of CG at 1291 cm^{-1} (the O = S = O stretching vibration of C-4 position of galactose), 929 cm^{-1} (C-O-C vibration mode of the 3,6-anhydro-D-galactose residue) and 844 cm^{-1} (the –O-SO_3 stretching vibration of C-4 position of galactose) are occurred in the MMT/CG composite hydrogel (Pereira et.al, 2003). The hydrogel and CG powder both had a broad absorption peak at 3500-3000 cm^{-1}, representing the -OH stretching mode. The absorption at 2920 cm^{-1} was observed due to C–O groups and the interlayer C–H stretching. The absorption at 1500 cm^{-1} was represented for the –CH_2 stretching. The absorption at 1080 cm^{-1} for glycosidic linkage, the absorption at 933 cm^{-1} for C–O of 3,6-anhydro-D-galactose and the absorption at 850 cm^{-1} for C–O–SO_3 of D-galactose-4-sulfate were obtained. The functional groups of Al-O and Si-O of MMT in the MMT/CG-composite hydrogel were occurred between 400 and 600 cm^{-1}, which was absent in the CG powder. (Hayati-Ashtiani, 2011). This can be proved by the formation of MMT/CG hydrogel.

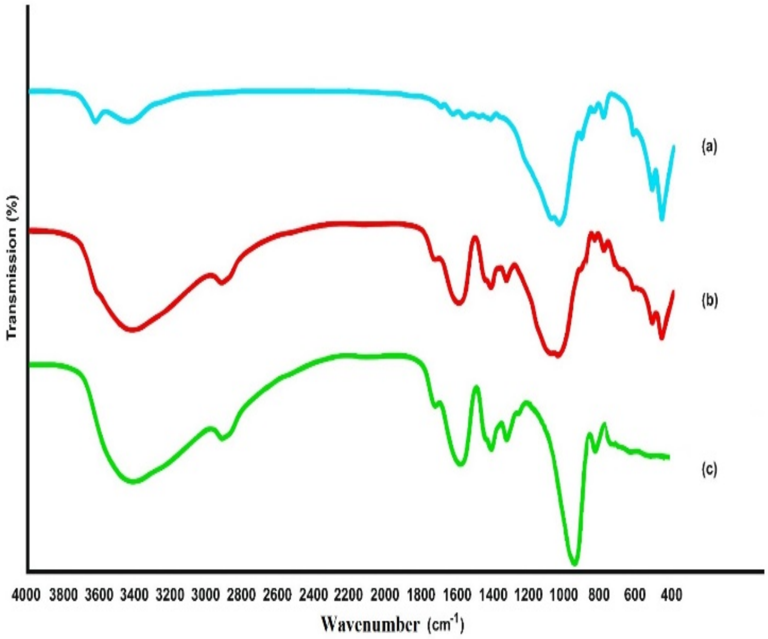


Figure 1. FTIR spectra of a) MMT powder, b) MMT/CG hydrogel, c) CG powder

XRD

The XRD diffractograms of the MMT powder, CG powder, MMT/CG-composite hydrogel (with MMT/CG mass ratio of 0.3:1 as representative sample) are shown in Figure 2. The sharp characteristic peak of MMT at nearly 6.00°2ϴ was observed, whereas this peak was not occurred in the diffractogram of CG powder and MMT/CG hydrogel. This can be explained by the connection of CG molecules into the MMT layer. Additionally, two peak were observed at 20-25°2ϴ for MMT powder, whereas CG powder, MMT/CG-composite hydrogel have a wider peak.

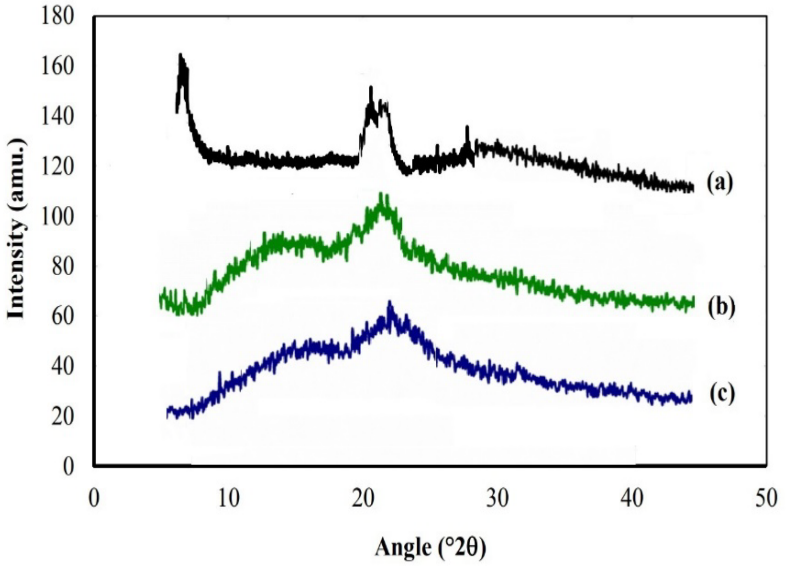
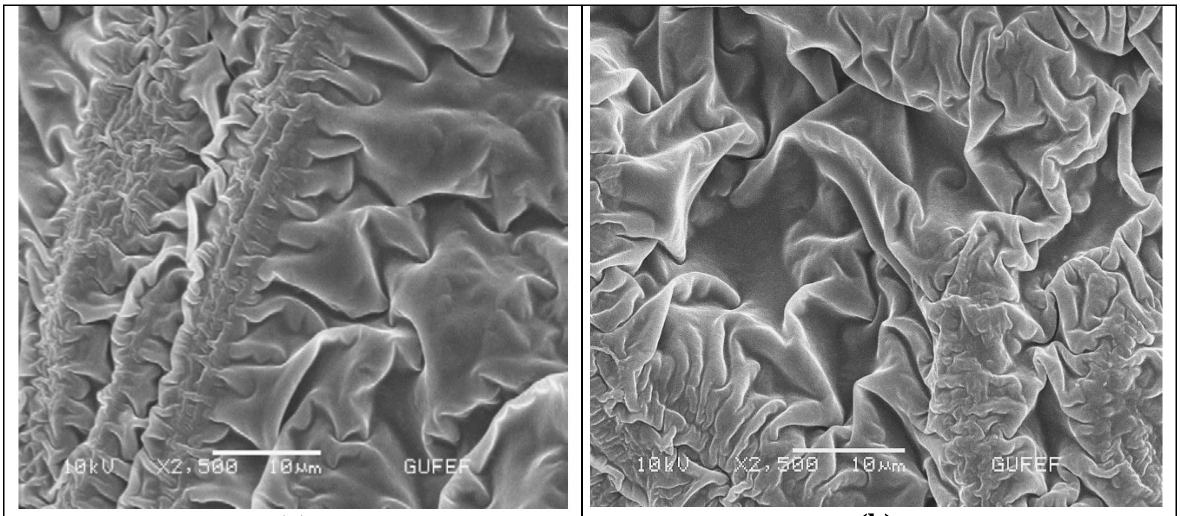


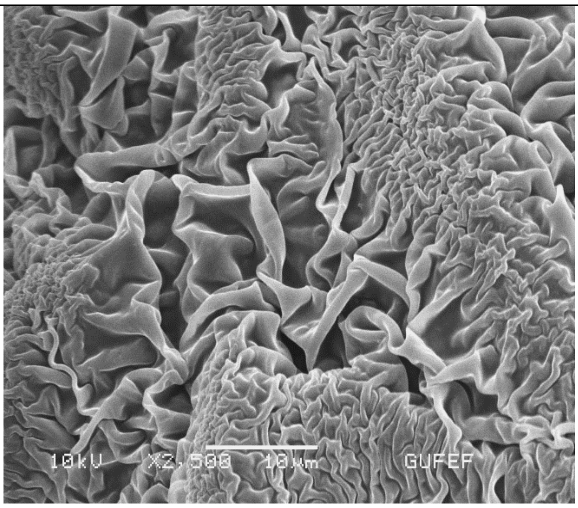
Figure. 2. XRD diffractograms of a) MMT powder, b) MMT/CG, c) CG powder

SEM

SEM images of MMT/CMC-composite hydrogels with different mass ratios are given in Figure 3. It was clearly seen that the surfaces of all hydrogels were rough. The most roughness was observed for MMT/CG (0.3:1) hydrogel. Surface roughness increased with increasing amount of MMT. This can be explained by the fact that the movement of the CG polymer chains may be interrupted by increasing the content of MMT, this causing the roughness to increase.



(a) **(b)**



(c)

Figure 3. SEM images of the MMT/CG-composite hydrogel at MMT/CG mass ratios of (a) 0.1:1, (b) 0.2:1 and (c) 0.3:1

Thermal Analysis

The thermal properties of hydrogels were researched by TGA analysis. The TGA thermogram of the MMT/CG hydrogel, compared with those of the CG and MMT powders and, is given in Figure 4. At 25°C to 800°C, the weight loss (%) of the MMT/CG hydrogel was lower than that of CG powder, which demonstrated a good thermal stability of the MMT/CG-composite hydrogel than that of the CG powder The results are compatible with the literature (Rojsitthisak et.al, 2019).

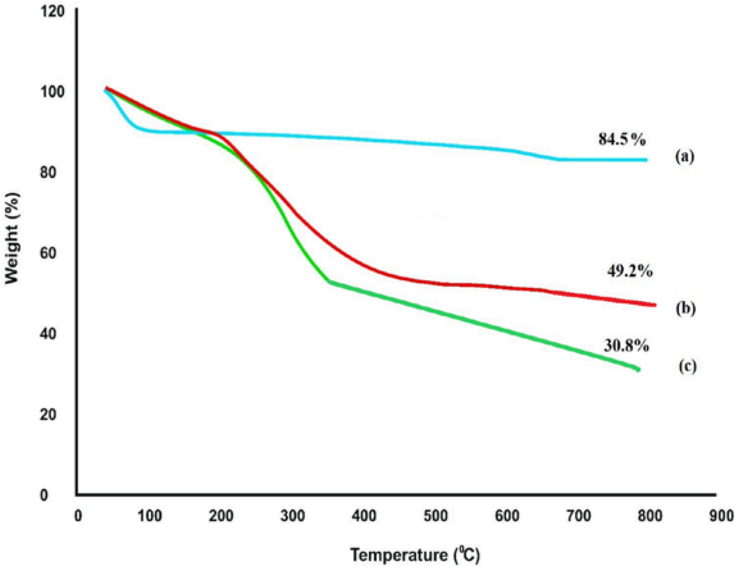


Figure 4. TGA thermogram of a) MMT powder, b) MMT/CG, c) CG powder

Adsorption Studies

The effects of contact time on the adsorption capacity (Q_t) of MMT/CG-composite hydrogels (mass ratio of MMT/CG 0.1:1 and 0.3:1) (initial concentration = 80 mg/L, without adjusted pH) were researched. While the contact time increased, the uptake rate of Cr (VI) ions accelerated and then, it reached a constant value. Firstly, the functional groups of the structure interact with metal ion easily. Thus, the adsorption became to increase. Over time, the adsorption rate slowed down and reached equilibrium. The adsorption capacity values increased gradually till 300 min and then the rate slowed down. The equilibrium adsorption value was found to be 71.4± 0.4 mg/g for MMT/CG hydrogel (0.1:1), while the equilibrium adsorption value was found to be 77.2 ± 0.3

mg/g for MMT/CG hydrogel (0.3:1). This difference can be explained by the increment of MMT made easier the penetration of water containing metal ion into the structure and so, the adsorption rate increased (Yang et. al, 2018).

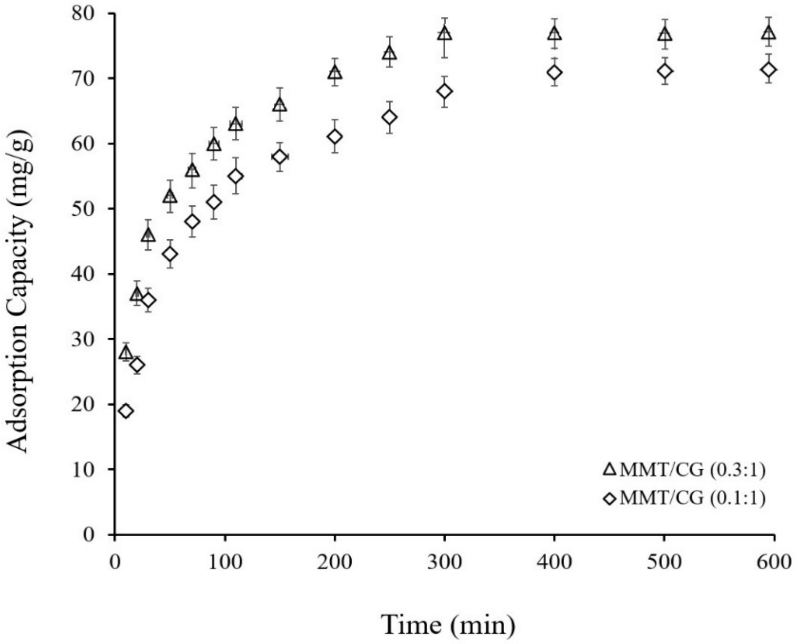


Figure 5. Effect of contact time on *Cr(VI)* metal ions adsorption capacity of MMT/CG hydrogel (initial metal ion concentration = 80 *mg/L*, without adjusted pH). Data are shown as mean ± SD of 3 independent trials.

Table 1. Equilibrium swelling degree of MMT/CG hydrogel beads

Samples	Swelling Degree (%)	Time
MMT/CG (0.1:1.0)	65.4± 0.2	600 min
MMT/CG (0.1:1.0)	72.4± 0.6	600 min

Note: Data are shown as mean ± SD of 3 independent trials

The effect of pH on the adsorption efficiency of MMT/CG hydrogel (0.1:1.0 and 0.3:1.0) is given in Figure 6. Samples were put into 50 mL of *Cr(VI)* solutions (80 mg/l) of different pH values. Initially, the adsorption increased speedily until pH 6. The maximum adsorption was obtained at pH 6 and then, it steadily decreased. Similar findings were reported in literature.

According to literature, *Cr(VI)* have various oxoanionic forms in aqueous solution at different pH. At pH 1.0, it is in the form of H_2CrO_4. Between pH 1–6, it is in the form of $HCrO_4^-$, which dimerizes to $Cr_2O_7^{2-}$ within the release of water molecules into the medium. Above pH 6, $Cr_2O_7^{2-}$ are reduced to form CrO_4^{2-}. formed, the electrostatic attraction increases thanks to this ionic form and the adsorption capacity also increases. Above pH 6, Cr (VI) is in the form of $Cr_2O_4^{2-}$. The positively charged adsorbent adsorbed Cr (VI) metal ions. After pH 6, two diavelent negative ions ($Cr_2O_4^{2-}$ and CrO_4^{2-}) exist in the medium. These ions alter the charge of the composite hydrogel from positive to negative, thus the electrostatic interaction between adsorbent to metal ions is decreased (Bhattacharyya & Sen Gupta, 2006; Khan et.al, 2017; Lei, Su, & Tian, 2018).

$2H_2CrO_4 \leftrightarrow 2H^+ + 2HCrO_4^-$ pH= 1

$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O$ pH 1-6

$Cr_2O_7^{2-} + H_2O \leftrightarrow 2CrO_4^{2-} + 2H^+$ pH> 6

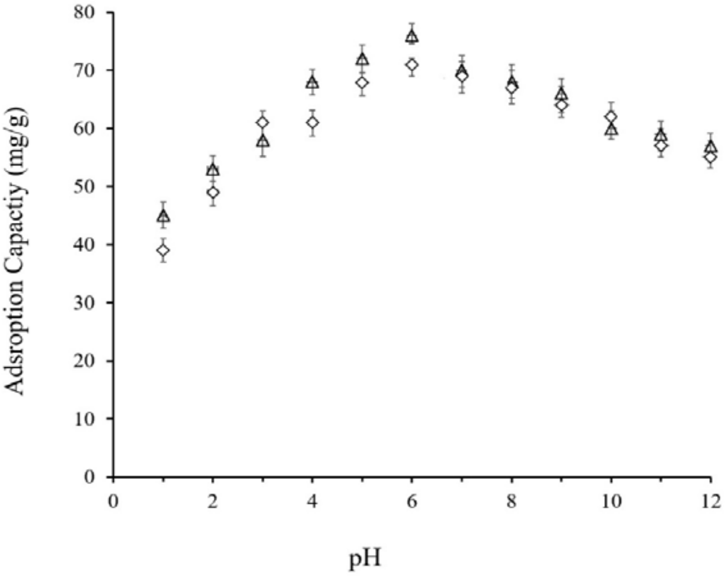


Figure 6. The effect of pH on the adsorption of *Cr(VI)* ions (under the conditions initial *Cr(VI)* concentration of 80 mg/L, temperature 25^{o}C in period of 600 min). Results shown are mean ± standard deviation, n = 3.

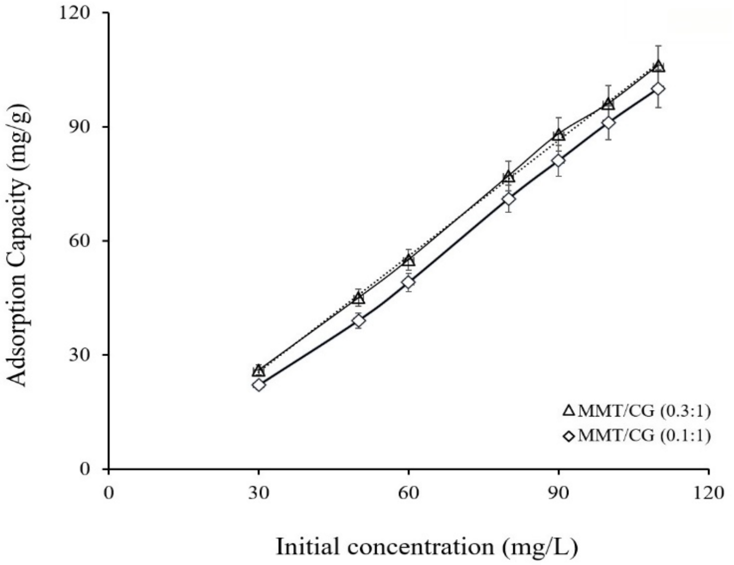


Figure 7. Effect of initial concentration on *Cr (VI)* metal ions adsorption capacity of MMT/CG hydrogel (pH = 7, contact time=600 min). Data are shown as mean ± SD of 3 independent trials.

The adsorption capacity (Q_t) of MMT/CG-composite hydrogels (mass ratio of MMT/CG 0.1:1 and 0.3:1) were investigated, the results are given in Figure 4. The adsorption capacity depends on initial concentration (*Ci*), in other words, *Qt* changed directly with *Ci* (Maity, & Ray 2016). The amount of adsorbed metal ions enhanced with increasing *Ci* value, so Q_t was increased. Q_t value of MMT/CG (0.3:1) changed from 26 to 106 mg/g, while Q_t value of MMT/CG (0.1:1) ranged from 22 to 100 mg/g. The highest Q_t value was obtained for MMT/CG (0.3:1).

An adsorption isotherm uses for the determination between the content of a metal ions adsorbed on adsorbent and the amount of the dissolved metal ions in solution at equilibrium. Additionally, it can describe the interaction between adsorbent and metal ions. Langmuir isotherm is commonly utilized to model the adsorption of metal ions on polymeric absorbent (Yu et.al, 2017; Yan et. al, 2018; Vilela et.al, 2019). According to this isotherm, adsorption takes place in certain homogeneous regions on the adsorbent, and no further adsorption takes place in the place occupied by the adsorbate.

Langmuir isotherm model was utilized for detecting the adsorption isotherm. The isotherm equation is given in below:

$$1/Qe = \frac{1}{Q_{max} x\, b\, x\, Ce} + \frac{1}{Q_{max}} \qquad (1)$$

where *Qe* is the adsorption capacity of the adsorbent at equilibrium, *Ce* is the metal ion concentration at equilibrium time, *b* is the Langmuir constant and Q_{max} is the maximum monolayer adsorption capacity. The correlation coefficient (R^2) was calculated for two samples from the graph. R^2 was found to be 0.9980 and 0.9984 for MMT/CG (0.1:1.0) and MMT/CG (0.3:1.0), respectively. The correlation coefficient close to 1 represents monolayer adsorption of metal ions on the adsorbent.

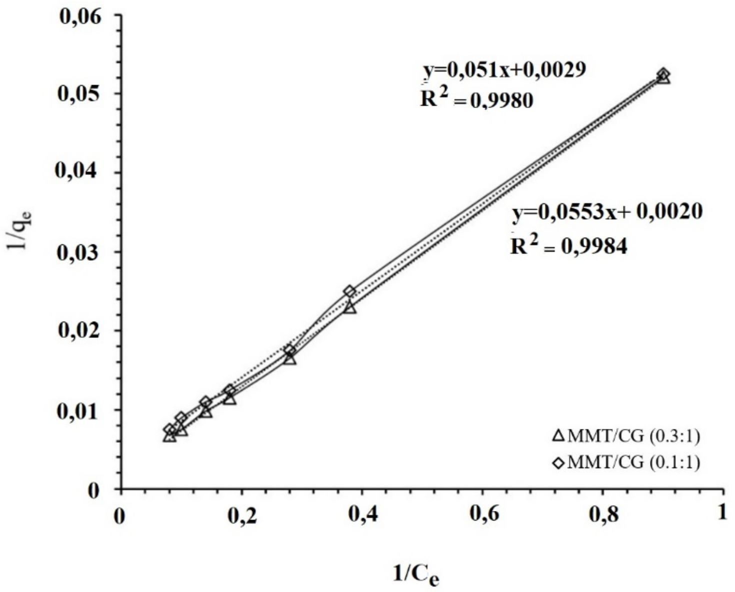


Figure 8. Langmuir isotherm for adsorption of Cr (VI) ions (under the conditions pH=6, temperature 25°C in period of 600 min).

Conclusions

Composite MMT/CG-hydrogels have the potential for being used as a polymeric adsorbent for the removal of *Cr(VI)* metal ions from aqueous solution. The maximum adsorption capacity of MMT/CG at a mass ratio of 0.3:1. The adsorption process can be described by the Langmuir isotherm model.

Scientific Ethics Declaration

The author declares that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the author.

Acknowledgements or Notes

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References

Ahmed, E. M. (2015). Hydrogel: preparation, characterization, and applications: A review. *Journal of advanced research*, *6*(2), 105-121.

Alemayehu, D. D., Singh, S. K. & Tessema, D. A. (2012). Assessment of the adsorption capacities of fired clay soils from Jimma (Ethiopia) for the removal of Cr (VI) from aqueous solution. *Universal Journal of Environmental. Research & Technology, 2*(5).

Bhattacharyya, K. G. & Sen Gupta, S. (2006). Adsorption of chromium (VI) from water by clays. *Industrial & Engineering Chemistry Research, 45*(21), 7232-7240.

Dakiky, M., Khamis, M., Manassra, A. & Mer'Eb, M. (2002). Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. *Advances in Environmental Research, 6*(4), 533-540.

Hayati-Ashtiani, M. (2011). Characterization of nano-porous bentonite (montmorillonite) particles using FTIR and BET-BJH analyses. *Particle & Particle Systems Characterization, 28*(3-4), 71-76.

Ianchis, R., Ninciuleanu, C. M., Gifu, I. C., Alexandrescu, E., Nistor, C. L., Nitu, S. & Petcu, C. (2020). Hydrogel-clay nanocomposites as carriers for controlled release. *Current Medicinal Chemistry, 27*(6), 919-954.

Islam, M. A., Angove, M. J. & Morton, D. W. (2019). Recent innovative research on chromium (VI) adsorption mechanism. *Environmental Nanotechnology, Monitoring & Management, 12*, 100267.

Kaşgöz, H. & Durmus, A. (2008). Dye removal by a novel hydrogel-clay nanocomposite with enhanced swelling properties. *Polymers for Advanced Technologies, 19*(7), 838-845.

Khan, T. A., Nazir, M., Ali, I. & Kumar, A. (2017). Removal of chromium (VI) from aqueous solution using guar gum–nano zinc oxide biocomposite adsorbent. *Arabian Journal of Chemistry, 10,* S2388-S2398.

Lei, Y., Su, H. & Tian, F. (2018). A novel nitrogen enriched hydrochar adsorbents derived from salix biomass for Cr (VI) adsorption. *Scientific reports, 8*(1), 1-9.

Maity, J. & Ray, S. K. (2016). Enhanced adsorption of Cr (VI) from water by guar gum based composite hydrogels. *International Journal of Biological Macromolecules, 89,* 246-255.

Pereira, L., Sousa, A., Coelho, H., Amado, A. M. & Ribeiro-Claro, P. J. (2003). Use of FTIR, FT-raman and 13C-NMR spectroscopy for identification of some seaweed phycocolloids. *Biomolecular Engineering, 20*(4-6), 223-228.

Rojsitthisak, P., Hansapaiboon, S., Sorasitthiyanukarn, F. N. & Limpanart, S. (2019). Montmorillonite/carboxymethylcellulose-composite hydrogel beads as biodegradable adsorbent for dye removal. *Maejo International Journal of Science and Technology, 13*(3), 170-184.

Sharma, G., Khosla, A., Kumar, A., Kaushal, N., Sharma, S., Naushad, M., ... & Stadler, F. J. (2022). A comprehensive review on the removal of noxious pollutants using carrageenan based advanced adsorbents. *Chemosphere, 289*, 133100.

Vilela, P. B., Dalalibera, A., Duminelli, E. C., Becegato, V. A. & Paulino, A. T. (2019). Adsorption and removal of chromium (VI) contained in aqueous solutions using a chitosan-based hydrogel. *Environmental Science and Pollution Research, 26*(28), 28481-28489.

Yan, E., Cao, M., Ren, X., Jiang, J., An, Q., Zhang, Z., ... & Zhang, D. (2018). Synthesis of Fe_3O_4 nanoparticles functionalized polyvinyl alcohol/chitosan magnetic composite hydrogel as an efficient adsorbent for chromium (VI) removal. *Journal of Physics and Chemistry of Solids, 121*, 102-109.

Yang, X., Li, F., Xia, M., Luo, F. & Jiang, Y. (2018). Investigation on the micro-structure and adsorption capacity of cellulosic biomass carbon based montmorillonite composite. *Microporous and Mesoporous Materials, 256,* 18-24.

Yu, P., Wang, H. Q., Bao, R. Y., Liu, Z., Yang, W., Xie, B. H. & Yang, M. B. (2017). Self-assembled sponge-like chitosan/reduced graphene oxide/montmorillonite composite hydrogels without cross-linking of chitosan for effective Cr (VI) sorption. *ACS Sustainable Chemistry & Engineering, 5*(2), 1557-1566.

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