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Preparation of Chitosan-Glycidyl Methacrylate Grafted Rice Straw Cellulose (Chi/GMAgCell) Composite Film for Cadmium Ions Removal from Water

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ABSTRACT

This research aims to develop an efficient adsorption material based on chitosan-glycidyl methacrylate grafted cellulose (Chi/GMAgCell) composite film as an adsorbent for the removal of Cd^{2+} ions from water. Cellulose was isolated from rice straw and grafted with glycidyl methacrylate to produce glycidyl methacrylate-grafted cellulose (GMAgCell). The GMAgCell was incorporated into a chitosan film (Chi-film) as a filler to form the Chi/GMAgCell composite film. To create Chi/GMAgCell composite films with high tensile strength and adsorption capacity (Qe) for Cd^{2+} ions, various chitosan-to-GMAgCell ratios were tested. These films were then evaluated using FTIR, XRD, SEM, TGA, and tensile strength analysis. The findings indicate that GMAgCell loading enhances the adsorption capacity (Qe) for Cd^{2+} ions, reaching 16.9 mg/g. Its adsorption equilibrium is achieved after 10 minutes. It also conforms to the pseudo-second-order (PSO) kinetic model, with R^2=0.9979. This process enhances the mechanical properties and thermal stability of the Chi-film composite while creating an affordable adsorbent material from agricultural waste.

1. INTRODUCTION

Water is a vital resource that sustains life on earth [1]. However, various anthropogenic activities, such as improper waste disposal, excessive use of pesticides and chemicals, industrial activity, and mining processes, have significantly contributed to water pollution [2-5]. Among the various pollutants, heavy metals (HMs) are particularly concerning because of their persistence in the environment and resistance to natural degradation [6, 7]. Globally, HMs pollution in water bodies has reached alarming levels. The World Health Organization (WHO) estimates that around 200 million people globally are exposed to excessive HM contamination in water [8], with cadmium (Cd) as a major contributor to this crisis [9]. Cd pollution is particularly severe due to its widespread sources, including battery production, pigments, and metallurgical industries [10]. The persistence and bioaccumulation of Cd in aquatic ecosystems necessitate urgent attention to its management and mitigation.

The consumption of water contaminated with HMs facilitates their bioaccumulation within biological systems, leading to significant health risks. These risks include carcinogenic effects, hematological disorders, damage to vital organs (kidneys, lungs, and liver), neurotoxicity, and, in severe cases, mortality [11-13]. It is crucial to develop effective and sustainable strategies to address this issue and to mitigate the environmental and health impacts posed by HM pollutants.

Various methods have been applied for the removal of Cd^{2+} ions from wastewater. Techniques such as chemical precipitation and ion exchange are constrained by pH limitations and generate toxic sludge, which requires further treatment [14, 15]. Membrane separation methods, while effective, are often associated with high operational costs and issues such as membrane fouling [16, 17]. Adsorption has gained widespread attention due to its versatility in material selection, ease of application, simplicity, and cost-effectiveness [18-21]. Commonly used adsorbent materials include activated carbon, polylactic acid from lactic acid, clay, zeolites, microorganisms and algae, cellulose, and chitosan [22-26].

Chitosan is a natural polymer belonging to the polysaccharide group, derived from the shells of crustaceans such as shrimp, clams, and crabs [27]. It exhibits excellent biocompatibility, biodegradability, and a range of functional properties, including haemostatic, anti-thrombogenic, immune-enhancing, and wound-healing activities [28]. Due to these characteristics, it has been explored extensively as an adsorbent for the removal of HM ions. This is attributed to the presence of active sites in chitosan such as -OH and $-NH_2$ groups. Studies have demonstrated that chitosan can effectively function as an adsorbent for Cd ion removal. However, its application as an adsorbent is limited by certain drawbacks, including low stability in acidic solutions, poor thermal resistance, limited surface area, and inadequate mechanical properties. To address these limitations, chitosan must be modified with other compounds to produce an adsorbent with great characteristics [29].

Cellulose is a promising material for modifying chitosan because of its high thermal and mechanical properties, as well as its abundant availability, biodegradability, and renewability [30, 31]. It can be sourced from various biomass, such as grass [32], sugarcane bagasse [33], rice straw [34], and bamboo [35]. While cellulose contains hydroxyl (-OH) groups that enable the adsorption of HM ions, their natural form has low adsorption capacity. Modifying cellulose can significantly improve its adsorption performance by introducing new functional groups [36]. One such modification method is grafting, using GMA as the grafting agent. GMA reacts with the hydroxyl groups of cellulose through its epoxy and acrylate groups, enhancing its properties [37].

Previous studies reported that GMA-g-Cell/Chi was successfully used as a sustainable adsorbent for methylene blue adsorption from wastewater with a maximum adsorption capacity (Qm) of 182.37mg/g [38]. Research [39] reported that chitosan bead-based adsorbent modified with glycine - PEDGE and Fe_3O_4 improves the ability of adsorbent to Cd^{2+} removal from aqueous solution [39]. Other studies have also reported the use of Chi-film composites filled with cellulose derived from sugarcane bagasse for methylene blue removal. These studies demonstrated that the Qm for methylene blue removal reached up to 3348.14mg/g [40]. While previous studies have demonstrated the potential of chitosan-based composites and GMA-grafted cellulose for dye and Cd ion removal from aqueous solutions, challenges remain in optimizing material performance under varying conditions. Furthermore, research on the synergistic effect of chitosan and GMA-grafted cellulose derived from rice straw in composite film form for Cd ion removal is still limited. This study seeks to bridge this gap by preparing and evaluating the performance of a Chi/GMAgCell composite film, offering a novel approach to enhance adsorption capacity and stability for Cd^{2+} ion removal from water.

2. MATERIALS AND METHODS

2.1 Materials

Rice straw was collected from Limpok Village, Aceh Besar Regency, Indonesia, after a few days post-harvest. Chitosan was purchased from Tokyo Chemical Industry Co., LTD. Glycidyl methacrylate (99% purity), NaOH, H_2SO_4, $Cd(NO_3)_2$, $K_2S_2O_8$ (Potassium persulphate/PSP), n-Hexane, C_2H_5OH, NaClO, and CH_3COOH and all other chemical reagent were purchased from Sigma-Aldrich (Singapore) with analytical grade, and distilled water.

2.2 Methods

2.2.1 Extraction of cellulose from rice straw

Cellulose extraction was followed by previous work with modifications [33, 41], Rice straw was crushed to reduce its size (±2cm), and the sample was then dewaxed using a mixture of n-hexane and ethanol (ratio 2:1) for 24 hours to eliminate wax, pigments, and oil from rice straw. This was followed by neutralization and drying at 50°C for 20 hours. Afterward, the dried sample underwent alkalization by being immersed in 12% NaOH solution at a ratio of 1:10 at 121°C with stirring at 150 rpm, for 1 hour, to remove lignin from lignocellulose structure through delignification, then the samples were rinsed using distilled water until pH neutral. After delignification, slurry then hydrolysis using H_2SO_4 (1:20), to remove hemicellulose followed by neutralizing using distilled water. Lastly, the slurry was bleached with 10% NaClO at 75°C, 100rpm for 60 minutes to remove impurities such as color and pigment in the slurry.

2.2.2 GMA grafted cellulose preparations

The GMAgCell was produced from rice straw using a similar procedure described in our previous work [37]. A total of 0.5g of Cell was introduced into 20mL of 0.0925 M PSP during the initiation stage and stirred at 100 rpm at 60°C for 1 hour under tightly sealed conditions. Subsequently, 20 mL of GMA was introduced, and the mixture was continuously stirred at 100rpm for 4 hours. The obtained product was then rinsed with distilled water followed by methanol to eliminate any residual monomers before being dried.

2.2.3 Chitosan and composite films preparations

Chitosan (1g) was dissolved in 100mL of 2% CH_3COOH, followed by stirring at 100rpm for 2 hours. The mixture was transferred into a film-casting mold (acrylic 17×12cm) and dried at 40°C in an oven for 48 hours [42]. To prepare the composite film, a total of 0.95g of chitosan was dissolved in 100mL of CH_3COOH (2%) while being stirred continuously for 2 hours at 100rpm to ensure full dissolution. Following this, 0.05g of GMAgCell was added to the chitosan solution and stirred at 100 rpm for another 2 hours to achieve proper dispersion. The final mixture was then cast into a mold and dried at 40°C for 48 hours, producing the Chi-GMAgCell composite film. A similar procedure was also performed to obtain composite films with different GMAgCell compositions, as described in Table 1.

Table 1. Experimental deign of chitosan and GMAgCell casting

Chitosan (g)	GMAgCell (g)	Composites
1.00	0.00	1
0.95	0.05	2
0.90	0.10	3
0.85	0.15	4

Notes: Total weight of chitosan +GMAgCell=1.00g

2.2.4 Characterization

Functional group examination was performed by Fourier transform infrared (FTIR) instrument with a range of 4000-400cm^{-1} (The Shimadzu FTIR 8400). The XRD was also performed on the samples to identify the crystallinity of each sample obtained, measured at a 2θ=0-70° with the source of ray from a Kα (Cu) 1.54. The thermal behaviour of samples is determined using a TGA instrument to observe changes in sample mass and is analyzed with temperature changes. Lastly, the surface of the samples was analyzed using SEM.

2.2.5 Adsorption study

Into 25mL of $Cd(NO_3)_2$ (35ppm) in Erlenmeyer flask, a total of 0.1g of prepared composite film (1×1cm) was introduced. It was agitated at 200rpm for 30 minutes, followed by filtration. The absorbance of the filtrate was then analyzed using an AAS spectrophotometer. The final concentration of Cd metal ions was calculated based on a calibration curve. The absorption capacity for Cd metal ions was calculated. The procedure was performed for the Chi-film and the three composite films. The adsorbent with the highest Qe was evaluated with variations of contact times (5, 10, 20, 30, and

40 minutes), pH (4, 6, 7, 8, and 10), and Cd metal ions concentration.

3. RESULT AND DISCUSSIONS

3.1 Influence of GMAgCell on tensile strength and Cd metal ions adsorption capacity of composite films

The evaluation of composite films with varying GMAgCell compositions revealed their impact on Qe and tensile strength, as presented in Figure 1. Among the tested formulations, composite 3, composed of 0.90g chitosan and 0.10g GMAgCell, exhibited the highest performance in terms of both Cd ion adsorption capacity and mechanical strength. The inclusion of GMAgCell as a filler notably improved the mechanical properties of the Chi-film, with a slight improvement in adsorption capacity. This improvement is due to the strong hydrogen bonding between the filler and the matrix, which enhances the tensile strength. However, an excessive amount of filler, as observed in Film 4, led to diminished performance in both adsorption capacity and tensile strength. This decline was likely caused by agglomeration due to dominant cohesive forces, which weakened the interaction between the matrix and filler [43]. These findings suggest that the balance between filler content and film properties is critical. Accordingly, Film 3 was selected as the optimal composite for further study on Cd ion adsorption. While the findings emphasize the benefits of balanced filler content, it is essential to consider that excessive reliance on fillers may lead to diminishing returns in performance, as seen in other composite materials [44, 45].

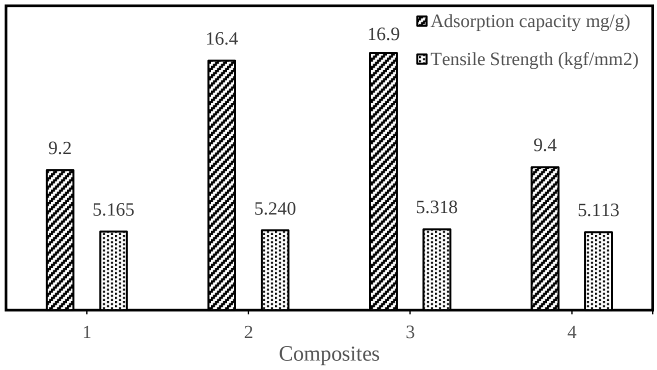


Figure 1. Tensile strength and Cd metal ions adsorption capacity (Qe) of Chi/GMAgCell films with various compositions of chitosan and GMAgCell

3.2 Characterizations

FTIR spectra of Chi-film, Chi/GMAgCell composite film, and GMAgCell are presented in Figure 2. An absorption band at a wavenumber of 3446cm^{-1} in Chi-film (Figure 2(a)) indicates the stretching vibration of -NH_2 and -OH groups. This absorption band shifts to wavenumber 3465 cm^{-1} in Figure 2(b) which shows that the process of modifying chitosan with GMAgCell occurred in the -OH group. It is also confirmed by the shift in the -OH absorption band GMAgCell (Figure 2(c)) [38].

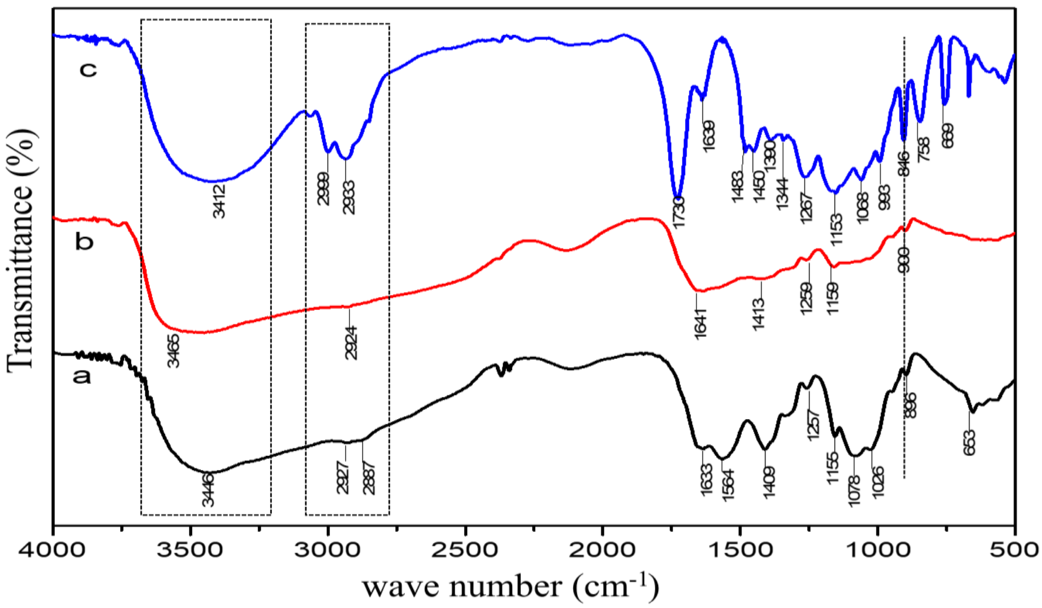


Figure 2. FTIR spectra analysis of (a) Chi-film, (b) Chi/GMAgCell composite film, and (c) GMAgCell

The wavenumber 2927cm^{-1} in Figure 2(a) relates to the CH stretching vibration. This absorption band is observed at wavenumbers 2924cm^{-1} and 2933cm^{-1} in Figure 2(b) and Figure 2(c), respectively. Figure 2(c) shows the absorption band at wavenumber 1730cm^{-1} indicating the C=O stretching vibration of the ester. The absorption band at 846cm^{-1} that belongs to epoxy groups stretching vibration of GMAgCell (Figure 2(c)) has disappeared in the Chi/GMAgCell composite film (Figure 2(b)) because the epoxy ring also acts as a crosslinker in the composite film [46].

The diffractograms of Chi-film, GMAgCell and Chi/GMAgCell composite film are shown in Figure 3. Figure 3(a) shows the semi-crystalline structure of Chi-film. Chitosan molecules can form semi-crystalline structures due to the hydroxyl and amine groups in chitosan molecules generate strong intermolecular and intramolecular hydrogen bonds [47].

The Chi-film diffractogram exhibits typical peaks at 2θ=11.37° and 17.93°. The intensities of these peaks decreased after the Chi-film was combined with GMAgCell to form Chi/GMAgCell composite film (Figure 3(b)). The presence of GMAgCell in Chi-film has disrupted the molecular order of chitosan, thereby reducing crystallinity. Although GMAgCell had a relatively higher peak intensity (Figure 3(c)), when it was combined with chitosan, it could not increase the crystallinity of the Chi-film. This reduction in crystallinity provides an advantage for the use of the film as an adsorbent by making it easier for the adsorbate to interact with the active sites in the adsorbent.

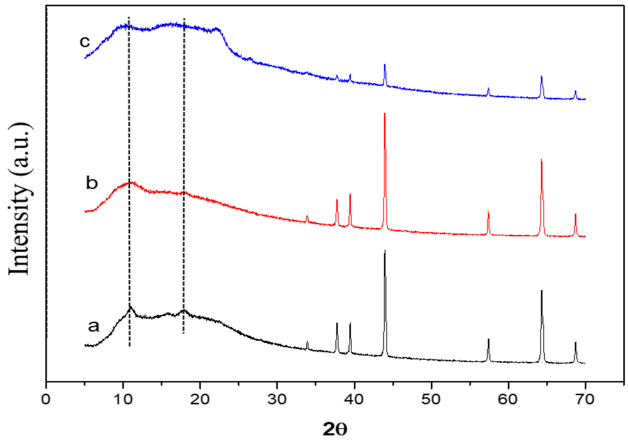
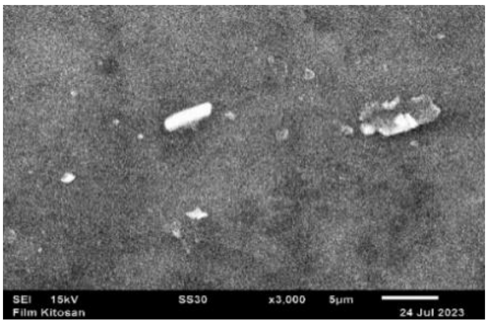
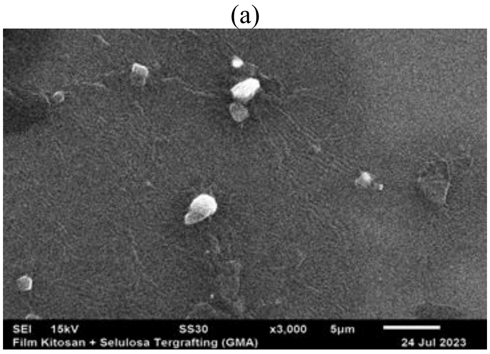


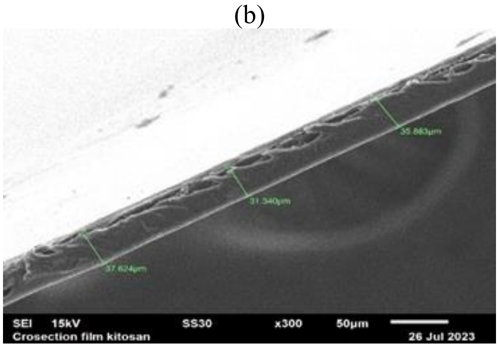
Figure 3. XRD diffractograms of (a) Chi-film, (b) Chi/GMAgCell composite film, and (c) GMAgCell



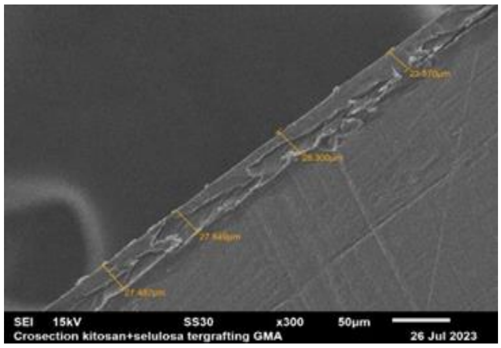
(a)



(b)



(c)



(d)

Figure 4. SEM morphology of (a) Chi-film surface, (b) Chi/GMAgCell composite film surface, (c) cross-section of Chi-film, and (d) cross-section of Chi/GMAgCell composite film

SEM morphology of the Chi-film surface with a magnification of 3000× (Figure 4(a)), shows a smoother surface than the Chi/GMAgCell composite film (Figure 4(b)). However, it was also observed chitosan particles which were not completely dissolved. The morphology of Chi/GMAgCell composite film shows a rougher surface due to the presence of GMAgCell particles as a filler of Chi-film. Films with rougher surfaces have better adsorption capacity of Cd metal ions because the polymer chains are relatively open and easily accessible for the adsorbate. Figures 4(c) and 4(d) show the Chi/GMAgCell composite film has a smaller cross-sectional area compared to the Chi-film. A smaller cross-sectional area will have a larger contact surface area so that it can increase the adsorption capacity.

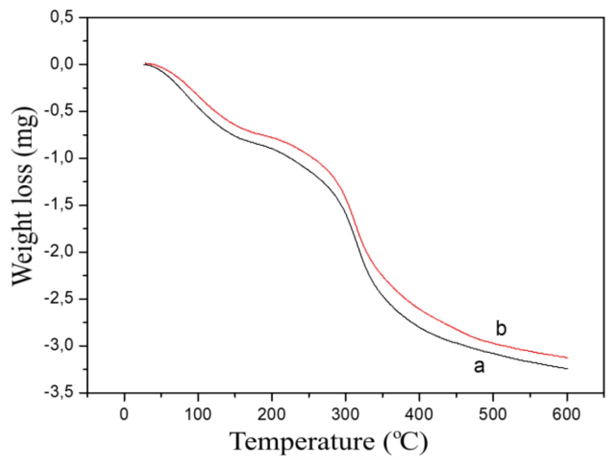


Figure 5. TGA curve of (a) Chi-film and (b) Chi/GMAgCell composite film

The thermogram of the composite film obtained is presented in Figure 5. Thermograms of Chi-film and Chi/GMAgCell composite film show stages of the thermal event. The first stage in these two films occurs at a temperature of 50 - 100°C, which shows the process of losing water from the sample. In the Chi-film (Figure 5(a)), the second stage was the sample degradation process, which started at 232°C with a total weight loss of 70.391%. This was due to the decomposition of chitosan through depolymerization of its chains, involving processes such as dehydration, delamination, deacetylation, and cleavage of glycosidic bonds [48]. The second stage of the Chi/GMAgCell composite film (Figure 5(b)) started at 241°C with a total weight loss of 66.580%. The third stage began at a temperature of 363°C and 369°C for Chi-film and Chi/GMAgCell film, respectively, which was the process of oxidation followed by the breakdown of carbon into gas with a low molecular weight. These findings show that the effect of GMAgCell added as a filler to the Chi-film enhanced its thermal properties.

3.3 Adsorption study

An adsorption study was conducted for Cd metal ions adsorption by Chi/GMAgCell composite film with various pH, initial concentration of Cd metal ions solution, and contact time. Figure 6 shows the impact of changing the contact time on the Qe of Cd metal ions. The adsorption capacity first rose with contact time and reached equilibrium after ten minutes. After this point, the adsorption capacity stabilized, with only a slight decrease observed, likely due to the desorption of previously adsorbed ions caused by the stirring during the adsorption process. This rapid attainment of adsorption equilibrium indicates that the Chi/GMAgCell composite film exhibits fast adsorption kinetics, making it a promising candidate for dynamic water treatment systems. The ability to reach equilibrium within a short time frame (10 minutes) suggests that the composite material can efficiently remove Cd metal ions in real-time water treatment applications, providing an effective solution for removing HMs from contaminated water.

Figure 7 shows the adsorption of Cd metal ions by Chi/GMAgCell composite film at various pH. At acidic pH, the Qe was low and increased by increasing pH (basic solution). It was due to an acidic solution containing a high amount of H^+ ions that strongly compete with Cd metal ions to bind with the negatively charged active sites (functional groups) on the adsorbent surface. At higher pH (basic), competition of H^+ ions with Cd metal ions decreases, thereby increasing the Qe of Cd metal ions [49]. Moreover, at high pH active sites of adsorbent become more negatively charged, thereby increasing the electrostatic attraction between Cd metal ions and the adsorbent. However, when the pH was too basic (pH>10), the precipitation could occur from dissolved hydroxide complexes; this phenomenon inhibited the adsorption process [50]. The highest Qe of Cd metal ions adsorption by Chi/GMAgCell composite in this work was obtained at pH 8.

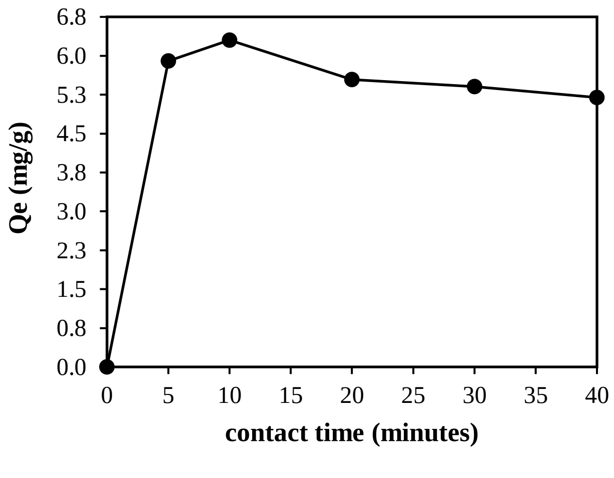


Figure 6. The Qe of Cd metal ions adsorption by Chi/GMAgCell composite film at various contact times

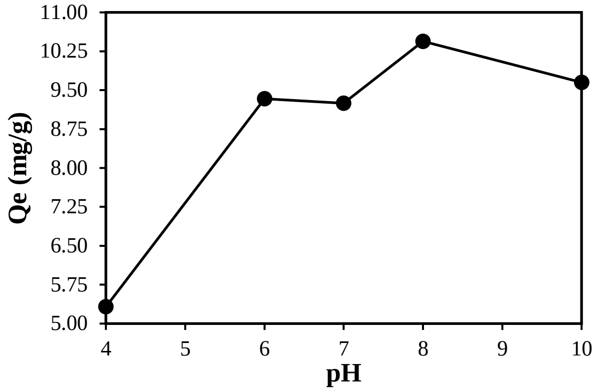


Figure 7. The Qe of Cd metal ions adsorption by Chi/GMAgCell composite film at various pH

Table 2. Adsorption kinetic parameters for Cd metal ions adsorption by Chi/GMAgCell film composites

Parameter	PFO	PSO
Qe	0.936mg/g	5.181mg/g
k	0.0125mg/g/min	0.231mg/g/min
R^2	0.6789	0.9979

Note: PFO and PSO- pseudo-first-order and pseudo-second-order, respectively

Using the pseudo-first-order (PFO) and PSO kinetic models, the kinetics of Cd metal ion adsorption by the Chi/GMAgCell composite films were investigated. Table 2 displays the parameters derived from these models. The PFO kinetic model assumes that physical adsorption takes place, with the adsorption rate being proportional to the number of available adsorption sites. This model is commonly used to describe systems where weak interactions, such as van der Waals forces, dominate the adsorption process.

However, according to the PSO kinetic model, chemical adsorption, which includes valence forces and potentially the creation of surface coordination bonds between the adsorbent and the adsorbate, controls the adsorption process. Higher correlation values (R^2), which show a better match between the experimental data and the PSO model, suggest that chemisorption processes are primarily responsible for the adsorption of Cd metal ions onto the Chi/GMAgCell composite.

According to Table 2, the PFO kinetic model's correlation coefficient (R^2) value is 0.6789, which is less than that of the PSO kinetic model. Hence, the adsorption process of Cd metal ions by Chi/GMAgCell composite film may be adequately described by the PSO kinetic model. According to this PSO model, metal ions attach to the adsorbent surface by forming chemical bonds, such as coordination covalent bonds, in a process known as chemisorption. The pseudo-second-order kinetic model's Qe value of 5.181mg/g is comparable to the experiment's Qe value of 5.45mg/g. The adsorption isotherm of Cd metal ions adsorption by Chi/GMAgCell composite film was described by the isotherm models (Langmuir and Freundlich), as shown in Table 3.

Using the Langmuir and Freundlich isotherm models, the adsorption of Cd metal ions onto the Chi/GMAgCell composite film was evaluated. The Langmuir isotherm model indicated a maximum adsorption capacity (Qm) of 4.83mg/g and a Langmuir constant (b) of -0.036. In contrast, the Freundlich isotherm model produced a Freundlich constant (K_f) of 250.67 and an adsorption intensity (n) of -1.26.

Table 3. Isotherm models study for Cd metal ions adsorption by Chi/GMAgCell composite film

Model	Parameter	Value
Langmuir isotherm	Qm (mg/g)	4.83
	b	-0.036
	R^2	0.8992
Freundlich isotherm	K_f	250.67
	n	-1.26
	R^2	0.9363

The Freundlich isotherm model outperforms the Langmuir isotherm model in terms of fitting the experimental data, as indicated by the R^2 values. This suggested that the adsorption of Cd metal ions by the Chi/GMAgCell composite film align more closely with the Freundlich isotherm model. While the Monolayer adsorption on a homogeneous surface with constant adsorption energies is assumed by the Langmuir model. The Freundlich model is best fits for describing adsorption on heterogeneous surfaces, where adsorption energies vary and physical adsorption prevails.

In this study, the negative n value (-1.26) suggests that the adsorption does not strictly follow the conventional Freundlich interpretation. While typically, n>1 indicates favorable adsorption with chemical interactions, and n<1 implies predominant physical adsorption, the negative n value here might reflect an unusual adsorption behaviour or inconsistencies that warrant further investigation. Despite this anomaly, the Freundlich model suggests the adsorption takes place on a heterogeneous surface with energy sites that vary in strength, aligning with the structural heterogeneity of the Chi/GMAgCell composite.

4. CONCLUSIONS

The incorporation of GMAgCell as a filler into chitosan significantly enhanced the performance of the composite film. GMAgCell loading has improved the adsorption capacity of the composite film by 83.696% and improved its tensile strength by 2.962%, making the composite more robust and effective. It also escalated the thermal stability of the Chi-film, contributing to its suitability for practical applications. The optimum conditions for Cd ion adsorption by the Chi/GMAgCell composite were achieved at a contact time of 10 minutes and a pH of 8. The adsorption process was best described by the PSO kinetic model, and adsorption isotherm data followed the Freundlich model, suggesting heterogeneous adsorption sites on the composite surface.

This study demonstrates that the Chi/GMAgCell composite film offers a sustainable, efficient, and cost-effective method for removing Cd metal ions from aqueous solutions. Its rapid adsorption kinetics and enhanced mechanical and thermal properties make it particularly suitable for industrial wastewater treatment with high concentrations of Cd metal ions pollution, offering potential for large-scale applications in water purification.

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