Microwave Assisted Synthesis of Xanthan gum-cl-Dimethyl acrylamide hydrogel based Silica hydrogel as Adsorbent for Cadmium (II) Removal

Edwin Makhado, Sadanand Pandey, Misook Kang and Elvis Fosso-Kankeu

Abstract**—**The present work highlights the synthesis of xanthan gum-cl-Dimethyl acrylamide hydrogel containing silica via microwave assisted method,in which N, N'-methylene bis-acrylamide (MBA) and ammonium persulfate (APS) were used as crosslinker and initiator, respectively. Silica was incorporated into the hydrogel matrix during the grafting reaction. The formation of XG-cl-DMAA/SiO_2hydrogel nanocomposite under optimized reaction conditions was verified by the infrared spectra (FTIR) and Scanning electron microscopy (SEM). XG-cl-DMAA/SiO_2hydrogel nanocomposite was used for adsorption of Cd^{2+} ions from aqueous solution. The Cd^{2+} ions adsorption was measured by inductively coupled plasma mass spectrometry. The factors influencing adsorption capacity of the absorbents such contact time, and initial dye concentration were investigated via a batch adsorption system. The maximum adsorption capacity, q_{max}, of 150.7 mg/gat 30°C was calculated based on the Langmuir isotherm. Heavy metal adsorption data fitted well to the pseudo-second-order model and equilibrium data were best described by Langmuir model.

Keywords**—** Xanthan gum; hydrogel nanocomposite; Microwave irradiation; Adsorption; Isotherm

I. INTRODUCTION

The steady growth of industrialization, results in the excessive releaseof various types of pollutants into water sources which is a major environmental problem. Toxic heavy metals such as Cd^{2+}, Cr^{6+}, Pb^{2+}, Hg^{2+}, Cu^{2+} and As^{3+} are continuously discharged from various industries like tanneries, metal plating, battery manufacturing, mining operations, printing and pigment and oil refining. Some of these metal ions are resistant of biological degradation and can accumulate in humans, threatens to cause serious diseases and disorders [1].

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Different researchers have employed various techniques for the removal of synthetic dyes and heavy metal ions from aqueous medium [2-4]. These methods include coagulation–flocculation, reverse osmosis, membrane separation, electrochemical treatment, photocatalysis, solvent extraction, oxidation–reduction, and adsorption [2-5]. The adsorption is globally recognized as the most promising technique for the removal of heavy metals and dyes from the wastewater due to its efficiency and cost-effective nature [5-9].

In this concern, the use of low cost hydrogels with porous structure attract special attention and gaze at as a good candidate for water remediation due to their three-dimensional crosslinked structure that can swell in water and trap the solute materials. Biopolymers are playing a vital role in many application of nanotechnology [10-19]. Water purification is among the one out of many application. In addition, application of polymeric hydrogels as adsorbents for effective removal of toxic metal ions has been considered by various researchers because of characteristic properties such, high adsorption capacity, and chemical stability as well as ionic functional groups which can remove metal ions from wastewater. Other characteristic properties which make hydrogels to stand out among other adsorbent materials are the ability of the incorporation of various chelating groups into the polymeric networks, recovery capacities and regeneration for repeated recycles [20]

In recent years, hydrogels based on organic/inorganic (O/I) hydrogels nanocomposite have been employed as adsorbents to remove heavy metals and dyes from wastewater. Some research works have reported on developing hydrogels nanocomposite because of their enhanced mechanical/thermal stability and swelling properties when compared with the hydrogels without additives [21]. In this direction, inorganic components such carbon-based, montmorillonite, polymeric, ceramic, and metallic nanomaterials [22-24] are introduced in the hydrogel polymeric matrix for the engineering of hydrogels nanocomposite. Silica (SiO2) based nanocomposites have attracted great attention because they are easy availability, low-cost, and effortless surface modification [25, 26] Ghoraiet al., reported the nanocomposite based on nanosilica for removal of Pd2+ ions from aqueous solutions [27]. Pourjavadi et al., prepared chitosan-g-acrylic acid based modified nanosilica hydrogel nanocomposite for heavy metal ion removal [28].

Very recently, gum xanthan- and SiO2-based hybrid

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nanocomposites have been used as adsorbents for the removal of dyes and heavy metal ions from aqueous solutions. To the best of our knowledge, no similar work have been reported based on the adsorption performance of XG-cl-DMAA/SiO2hydrogel nanocomposite can be found in literature so far. The present work investigates the efficiency of the XG-cl-DMAA/SiO2hydrogel nanocomposite in the removal of Cd2+ ionsfrom aqueous solutions. The equilibrium removal efficiency was studied using isotherm models and kinetic parameters of the adsorption process.

II. Materials And Method

A. Materials

The biopolymer, xanthan gum (XG) from *Xanthomonas campestris* was supplied by Sigma-Aldrich (South Africa). Dimethyl acrylamide (DMAA, 99%) monomer was obtained from Sigma-Aldrich (Netherlands) and acetone was procured from Merck (South Africa)and was used without further purification. Initiator ammonium persulfate (APS) (≥98%; 248614), the cross linker N, N'-methylene bis-acrylamide (MBA), 99%, cadmium nitrate tetrahydrate, 98%, were obtained from Sigma-Aldrich (South Africa) and used without further purification. Sodium hydroxide (NaOH) and Hydrochloric acid (HCL) were procured from Merck (South Africa). All reagents used were of analytical grade. For all the experiments, deionized (DI) water was used. The stock solution of Cd^{2+} ions(1000 mg/L) was prepared by dissolving an appropriate amount of cadmium nitrate tetrahydrate in 1 L of deionized water, and the stock solution was further diluted for batch experiments.

B. Characterization

Samsung (Model No. ME9114W1; 1500 W, Made: Malaysia) domestic microwave oven having 2450 MHz microwave frequency and a power output from 0 to 1000 W was used for synthesis of hydrogel nanocomposite. The pH of the reaction mixture was adjusted using HCl or NaOH (0.1 M). The pH measurements were made with HI 9811-5/HI 1285-5 (Romania). FTIR spectra were recorded on a Spectrum-100 Perkin Elmer, USA, in the spectral range of 4000 to 400 cm^{-1} with a resolution of 4. The samples were compressed into pellets using spectroscopic grade KBr (Sigma-Aldrich, South Africa). The surface morphologies of the samples were examined by a scanning electron microscopy (SEM), (TESCAN, VEGA SEM) under a 20 kV electron acceleration voltage. To avoid charging these samples were coated with carbon.

C. Preparation of Silica oligomer

Tetraethoxysilane (2.5 mL) was dissolved in ethanol (2.5 mL). In a second solution 1.75 mL of 12N ammonium hydroxide was prepared independently. All the two solutions were emptied together into a reaction glass flask with 20 mL of deionized water and kept under tender blending for more than 18 hrs at room temperature to develop monodisperse SiO_2 particles inside the medium. The following blend was then be dissipated in air at 40 °C (4 h), 60 °C (5 h), 70 °C (3 h) and 80 °C for 1 h until a dry material, SiO_2 was acquired.

D. Synthesis of XG-cl-DMAA/SiO_2 hydrogel nanocomposite

A polymer matrix composed of XG-cl-DMAA was prepared by using MBA as crosslinker and APS as initiator in a domestic microwave. The grafting of DMAA onto XG in the presence of MBA cross linker by free radical co-polymerization technique. XG (0.1 g) was dissolved was homogenously dissolve in a 100 mL open beaker containing DI. Calculated amount of AA, MBA were added and APS was added in order to initiate the reaction of graft copolymerization. Then 0.1 g of SiO_2 was dispersed in 5 mL of DI water, and then sonicated for 5 min by using ultrasonicator, the SiO_2 solution was added to the graft copolymerization reaction in a 100 mL open beaker. The beaker was exposed under fixed microwave power for a definite time period in a domestic microwave oven with a microwave frequency of 2450 MHz. After desired time period, the XG-cl-DMAA/SiO_2 hydrogel nanocomposite was precipitated by pouring the reaction mixture into a large quantity of acetone and washed well to remove adhered homopolymer, if any is present along with graft copolymers. The precipitated copolymer was filtered and the copolymer samples obtained were finally dried under vacuum at 60 ◦C for >24**.**

E. Adsorption studies

Cd^{2+} sorption investigations were performed by the batch method. Adsorption examinations were carried out usingXG-cl-DMAA/SiO_2hydrogel nanocomposite as adsorbent on a temperature controlled incubator shaker set at 130 rpm kept up at 30 °C for 120 min. Here, known measures of adsorbents (25mg) were completely mixed with 20 mL of individual Cd^{2+}solutions, whose concentrations and pHs (5.0) were beforehand known. After the PE plastic bottles were shaken for the desired time, the suspensions were filtered through 0.45 µm PVDF syringe filters. The concentration of the unadsorbed Cd^{2+} ions left behind in each solution was analyzed using an inductively coupled plasma mass spectrometry. The equilibrium uptake was calculated using Equation (1)

$$qe = (Co - Ce) \times \frac{V}{W} \quad (1)$$

where, qe is the equilibrium capacity of Cd^{2+} ions on the adsorbent (mg/g), Co denotes the initial and the Ce denotes the equilibrium concentrations (mg/L) of Cd^{2+} ions, respectively. V is the volume of dye solution used (L) and W is the weight of adsorbent (g) used. All the batch experiments were carried out in triplicate and results represented here are the average of three readings.

III. Results And Discussion

A. FTIR-spectroscopy

The structural changes of XG and XG-cl-DMAA/SiO_2hydrogel nanocomposite were confirmed by FTIR spectroscopy and the results are presented **Fig. 1(a)**. Pure XG had the characteristic bands at 3246 cm^{-1}, 2932 cm^{-1}, and 1404 cm^{-1} due to the characteristic stretching vibration of both primary and secondary O-H bonds , -CH stretching of

alkyl group, and at 1404 cm^{-1} due to CH bending of methyl group, respectively. Additional characteristic absorption bands of the polysaccharide appear at 1023 cm^{-1}due to stretching of the C O bond [6].In the cases of XG-cl-DMAA/SiO_2hydrogel nanocomposite, a hump at 3142 cm^{-1}appeared in a broad absorption peak of XG after the surface-modification with DMAA/SiO_2. The band at 1643 cm^{-1}can be attributed to carbonyl of acrylamide. Furthermore, characteristic band at 1036 $cm^{-1}$is due to the stretching vibration of N-CH_3 [29]. These results indicated that DMAA was chemically grafted onto the XG.

B. Electron microscopy characterization

The surface morphologies of the XG and XG-cl-DMAA/$SiO_2$are depicted in **Fig. 1(b-c)**. SEM micrograph of the XG is shown in **Fig. 1(b)** and the granular morphology can be clearly seen which suggests the amorphous nature of the biopolymer [30-32]. The SEM of XG-cl-DMAA/SiO_2displays rough irregular surface morphology shown in **Fig. 1(b)**.The rough uneven surface morphology observed for XG-cl-DMAA/SiO_2 seems to have been covered by Cd^{2+} after the adsorption study. XG-cl-DMAA/SiO_2after adsorption had smooth homogeneous surface morphology which evidenced Cd^{2+} loading onto the of XG-cl-DMAA/SiO_2 hydrogel nanocomposite (**Fig. 1d**).

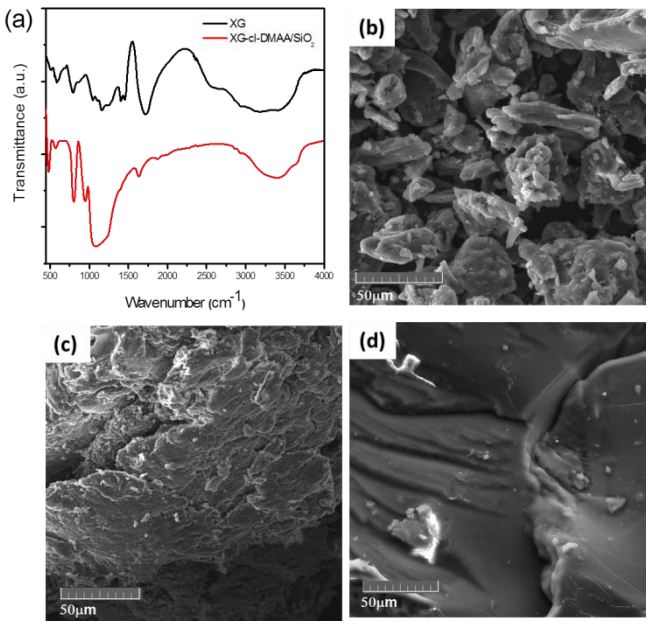

Fig. 1. Shows the (a) FT-IR spectra of the XG and XG-cl-DMAA/SiO_2, SEM image resolution at 600x of (b) XG; (c) XG-cl-DMAA/SiO_2 and (d) Cd^{2+} loaded XG-cl-DMAA/SiO_2.

C. Pseudo-first-order and the pseudo-second order equations

Cd^{2+} removal by XG-cl-DMAA/SiO_2hydrogel nanocomposite as a function of contact time was measured and the results are shown in **Fig. 2**.The kinetic parameters obtained at 100 mg/L concentration of Cd^{2+}areillustrated in **Table 1.** The Pseudo-first-order kinetic model of Langergren Equation (2) [33] and the Pseudo-second order kinetic Equation (3) [34] models are often used to govern the rate constant and to examine the mechanism of the adsorption process. Their linear forms can be expressed as:

$$\frac{\log(q_e - q_t)}{q_e} = \log q_e - \frac{k_1}{2.030} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k' q_e^2} + \frac{t}{q_e} \quad (3)$$

Where, qe (mg/g) is the adsorption capacity of XG-cl-DMAA/SiO_2 hydrogel nanocomposite in equilibrium; K_1 (min^{-1}) is the rate constant of the Pseudo-first-order model; and K_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order model. The experimental data in were fitted linearly by using Equation (2) and (3). These results indicated that the experimental data was in agreement with Pseudo-second-order kinetic model (R^2 = 0.997) for the adsorption of Cd^{2+} on XG-cl-DMAA/SiO_2 hydrogel nanocomposite compared to the Pseudo-first-order model (R^2 = 0.669). Furthermore, these results indicated that the adsorption of Cd^{2+} on XG-cl-DMAA/SiO_2 hydrogel nanocomposite was mainly a chemical process.

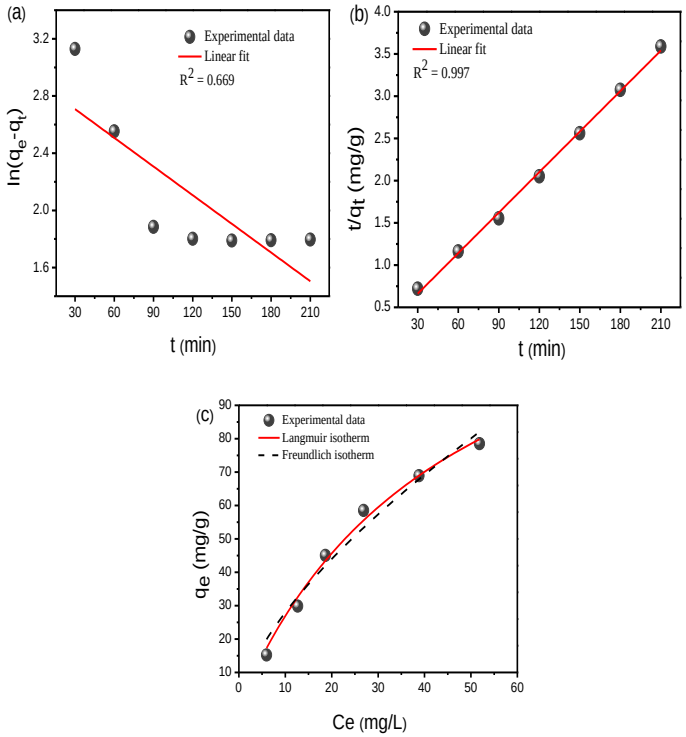

Fig. 2. Adsorption kinetics of Cd^{2+} onto according to (a) Pseudo-first-order model, (b) pseudo-second-order model, and (c) non-linear Langmuir and Freundlich isotherm model.

TABLE I KINETIC PARAMETERS FOR CD^{2+} ADSORPTION BY XG-CL-DMAA/SIO_2HYDROGEL NANOCOMPOSITE.

Pseudo-first-order			Pseudo-second-order		
qe (mg/g)	$k_1(min^{-1})$	R^2	qe(mg/g)	k_2(g(mg/min))	R^2
0.445	0.015	0.669	62.5	1.8935	0.997

D. Langmuir isotherm

Adsorption isotherm studies are remarkably significant to determine the efficacy of adsorption. Several adsorption isotherms initially used for gas phase adsorption are available and readily adopted to correlate adsorption equilibria in heavy metals adsorption. In this work, the adsorption isotherms were investigated using two equilibrium models, which are Langmuir and Freundlich isotherm models.

The Langmuir isotherm is based on the assumption that monolayer adsorption takes place on an adsorbent that have a structurally homogeneous surface, on which the binding sites have the same affinity for the adsorption, and no interaction occurs between adsorbates [35]. The equation representing nonlinear Langmuir isotherm model is given as:

$$qe = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (4)$$

where, qe is adsorption capacity at equilibrium (mg/g), Ce is equilibrium concentrations of adsorbate in liquid phases (mg/L), qmax is the maximum adsorption capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant related to the energy of adsorption (L/mg). Langmuir constants, K_L and q_{max}, can be obtained from the non-linear fit of qe versus Ce.

E. Freundlich isotherm

The Freundlich isotherm is based on the assumption that the adsorption process takes place on heterogeneous surfaces, and adsorption capacity is related to the concentration of dye at equilibrium [36]. The nonlinear Freundlich isotherm is expressed as:

$$qe = K_F Ce^{\frac{1}{n}} \quad (5)$$

Where, K_F and n are the Freundlich constants related to adsorption capacity and indicative of the energy or intensity of the reaction, respectively, qe and Ce are the adsorption capacity at equilibrium (mg/g) and equilibrium concentrations of adsorbate in liquid phases (mg/L), respectively. The Freundlich constants, K_F and n, can be obtained from the non-linear fit of qe versus Ce.

It is seen from **Table 2** that the correlation coefficient of Langmuir isotherm (R^2 = 0.989) models is more than that of Freundlich isotherm model (R^2 = 0.966). The adsorption isotherms of Cd^{2+} on XG-cl-DMAA/SiO_2 hydrogel nanocomposite indicated that Langmuir model more precise in evaluating the sorption equilibrium (see **Fig. 2(c)**). Langmuir model assumes that adsorption is monolayer coverage and the adsorption site on adsorbent surface is homogeneous [37-]. The maximum adsorption capacity Cd^{2+}on XG-cl-DMAA/SiO_2 hydrogel nanocomposite was found to be 150.7 mg/g.

TABLE II ADSORPTION ISOTHERM STUDY OF Cd^{2+} ADSORPTION BY XG-CL-DMAA/SiO_2 HYDROGEL NANOCOMPOSITE ACCORDING TO EQUILIBRIUM MODELS.

Langmuir isotherm			Freundlich isotherm		
qmax (mg/g)	K_L	R^2	n	K_F	R^2
150.7	0.027	0.989	1.527	6.185	0.966

IV. CONCLUSION

In this study, XG-cl-DMAA/SiO_2hydrogel nanocomposite was successfully synthesized by microwave irradiation method. A new type of XG-cl-DMAA/SiO_2hydrogel nanocomposite sorbent was developed for the removal of Cd^{2+} from the aqueous medium. Cadmium removal was investigated via a batch adsorption system. The adsorption process was reached at equilibrium state within 120 min at pH 5.The adsorption followed pseudo-second-order kinetic and Langmuir isotherm models. The maximum adsorption capacity Cd^{2+} on XG-cl-DMAA/SiO_2 hydrogel nanocomposite was 150.7 mg/g at 30°C.

CONFLICT OF INTEREST

The authors declare no competing financial interest.

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