Efficient Removal of Cationic Dye on *k*-carrageenan –based Hydrogel

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Abstract—In the present work, the synthesis of *k*-carrageenan –crosslinked poly(acrylonitrile co-acrylamide) hydrogel through copolymerization of acrylonitrile and acrylamide. The optimum conditions for the synthesis of *k*-carrageenan – crosslinked poly(acrylonitrile co-acrylamide) hydrogel were determined by varying several parameters such as monomers, cross linker, initiator and reaction time.

The structure and morphology of the synthesized hydrogel and the exposed hydrogel (containing Brilliant Green) were characterized by FT-IR and adsorption experiments were carried out using various adsorbent dosages. The adsorption kinetics results showed that the adsorption followed pseudo-second order, this implies that the adsorption of the dye took plase through chemisorption mechanism.

Keywords—Biopolymer; Hydrogel; Graft co-polymerisation; Adsorption

I. INTRODUCTION

Water contamination is a reoccurring issue, which is often not taken seriously and affects public health and the environment [1]. Worldwide water pollution has been the cause of multiple deaths and diseases, killing about 14000 people daily, that is approximately more than 5 million people yearly [2; 3]. This global environmental issue is caused by numerous pollutants that pollute water resources [1; 4-19].

Water pollution are mainly due to chemical contamination, from industrial or domestic effluents, agricultural fertilizers that contributes to eutrophication and untreated sewage and waste, that are discharged into the water sources [20].

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Water quality and water sources play a cardinal role in South Africa due to the physical shortage of clean and available water [21]. Multiple factors contribute to the growing shortage of water such as climate change within regions and infrequent rainfall [22]. Physical shortage of water could also be due to the increase in pollutants caused by mining industries, manufacturing industries, agriculture and untreated waste and sewage [21].

One of the largest water contamination contributors is the discharge of dyes into receiving water due to domestic and textile industrial pollution. Textile dyeing, the dyeing of material such as fabrics, fibers, cotton and yarns, is a major water contaminant which is unknown to most people [23; 24].

Dyes are classified into various classes mainly natural dyes and synthetic dyes [25]. The major sources of natural dyes are derived from plants but can also be derived from other natural resources and is broadly classified as animal, mineral and microbial dyes [26].

Synthetic dyes are made from organic molecules and are not found in nature and are therefore categorized as man-made dyes [27; 28].

The colored dye effluent that is discharged into the environment is toxic, causes skin allergies, is mutagenic to humans, carcinogenic and is harmful to aquatic life even at low concentrations [23; 29]. Adsorption is only as good as the adsorbent used in the adsorption process. Therefore, various adsorbents are available on the market which include clay materials, maize cob, starch, sawdust and hydrogels [30-32]. Different adsorbents will have different effectiveness, cost and will yield different results.

Adsorption technique will be used in this study to adsorb a cationic dye (Brilliant Green) on a k-carrageenan-crosslinked polyacrylonitrile co-polyacrylamide hydrogel.

The objectives in the study are the synthesis and characterization of the k-carrageenan–crosslinked (polyacrylonitrile co-polyacrylamide) hydrogel for dye removal from waste water.

II. Materials and experimental methods

A. Materials

Acrylamide, acrylonitrile, N, N'-methylenebis-acrylamide (MBA) and Brilliant Green were purchased from Sigma-Aldrich, in South Africa. Acetone was purchased from Rochelle Chemicals & Lab Equipment C.C, in South Africa. Ammonium persulphate (APS), k-carrageenan, sodium hydroxide (used to increase the pH) and hydrochloric acid (used to reduce the pH) were provided by the laboratory of the school of chemical and minerals engineering at the North-West university, in South Africa.

B. Synthesis of k-carrageenan based hydrogel

The k-carrageenan - crosslinked poly(acrylonitrile co-acrylamide) hydrogel was prepared through copolymerization, which entails the grafting of the acrylonitrile and acrylamide monomers by an ammonium persulphate initiator (APS) followed by crosslinking (in the presence of a crosslinker methylene bis acrylamide (MBA)) onto the biopolymer, k-carrageenan [32-35; 36].

For the synthesis of the hydrogel, 3 mL acrylonitrile and 0.5 g acrylamide were respectively dissolved in 2.0 mL and 5.0 mL distilled water, in 28 mL glass vials. The two solutions were added together into a 100 mL beaker and placed on a magnetic stirrer which stirred the solution for 5 minutes. The solution in the 100 mL beaker was continuously stirred at 750 rpm on the magnetic stirrer until all the reagents were added.

0.5 g of K-carrageenan was then dissolved in 10.0 mL warm distilled water in a 50 mL beaker. The dissolved k-carrageen was then added to the acrylonitrile and acrylamide reaction mixture, which was stirred for 5 minutes. After 5 minutes, 0.02 g of APS, dissolved in 10.0 mL distilled water in a 28 mL glass vial, was added to the reaction mixture and stirred for 1 minute. 0.03 g of MBA, dissolved in 5 mL distilled water in a 28 mL glass vial, was then added to the reaction mixture and was stirred for 5 minutes. Whilst stirring was taking place the temperature was maintained at room temperature, 25 °C. After the mixing of the chemical components, the hydrogel was poured out into a 100 mL Duran bottle and placed in the shaking incubator, for polymerization to take place, at a temperature of 65 °C and 180 rpm shaking speed.

The reaction mixture was then left for 5 hours in the mixing state, in the shaking incubator, where after the polymerization was completed and a hydrogel formed. The polymer hydrogel was taken out of the shaking incubator and 100 mL acetone was added to the polymerized hydrogel. The acetone that was added to the hydrogel made the cutting of the gel easy, making it possible to divide the gel into smaller fragments. The hydrogel was immersed in acetone for 12 to 15 hours, to remove excess and unreacted monomers.

After the washing process (hydrogel in acetone) the product was drained from the solution through a 11 cm filter paper (with a retention of 2.5 μm and a filtration speed of 124 seconds) and was then placed on a baking tray on top of a 32 cm filter paper (with a medium retention and flow speed of 11 μm). The baking tray with the product was placed in a hot air oven and was dried at a temperature of 50 °C to 60 °C, until a constant weight was achieved, and the hydrogel was dry enough to crush. Swelling studies were then done on the synthesized hydrogel to determine the swelling capacity of the hydrogel.

C. Preparation of dye solution

The dye solutions used in the adsorption process was prepared by diluting 100 mg of the specific desired dye in 1 L (100 ppm,) distilled water. 50 mL of this dye stock solution was then poured into 250 mL Erlenmeyer flasks and was further used in the adsorption process [4].

D. Adsorption of Brilliant Green dye

Adsorption was carried out for the removal of brilliant green from solutions using the hydrogel. 50 mL of the stock solution was added to a 250 mL erlenmeyer flask together with 0.04 g of the adsorbent, the solution was then placed in the shaking incubator at a temperature of 25 °C for 60 minutes at a shaking speed of 160 rpm [37]. After 60 minutes in the shaking incubator 20 mL of the 50 mL solution was poured into a centrifuge tube, then centrifuged (Rotofix 32 A) for 10 mins at a speed of 4 000 rpm. After the centrifugation process, the liquid from the centrifuge tube was transferred into a clean centrifuge tube, without transferring any solid gel particles. 3 mL of the clean solution, without particles, were transferred into a cuvette and placed into the Genesys UV/Vis spectrophotometer, recording the absorbance at λ_{max}= 425 nm, the absorbance of the dye that was measured were then related to concentration (mg/L) using standard calibration curves.

Equation1 and Equation 2 were used to determine the adsorption efficiency (percentage of dye removal) of the hydrogel and the adsorption capacity (q_e) [37]:

$$\% \ Removal \ of \ dye = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

C_0 is the initial concentration of the dye solution (mg/L), C_e is the final concentration of the dye solution (mg/L), V is the dye solution volume (L) and m the weight (g) of the dry adsorbent [37-45].

Equation3is the adsorption capacity (q_t (mg/g)) at time t (min), the adsorption capacity is used to

determine the concentration of Brilliant Green after recorded time intervals.

$$q_t = \frac{C_0 - C_t}{m} \times V \qquad (3)$$

C_t is the remaining dye concentration in the solution at a given time.

The adsorbent studies were done on the best synthesized hydrogel, together with the BG dye. The best adsorption conditions were obtained by varying different experimental parameters and the effects thereof. Adsorption of the dye onto the hydrogel was therefore studied by varying different parameters such as; time (in the shaking incubator) over a range of 10-180 min, adsorbent dose over a range of 25 mg – 70 mg. The experiments were carried out in duplicate to ensure repeatability.

E. CHARACTERIZATION (INSTRUMENTATION)

FTIR

FT-IR spectra of *k*-carrageenan -crosslinked poly(acrylonitrile -co-acrylamide) based hydrogel and *k*-carrageenan based hydrogel loaded with BG dye samples were tested using the Thermo Fisher Smart iTR, Nicolet Is10 spectrophotometer made; with a frequency range of 650 – 4000 cm^{-1} [37-44].

III. RESULTS AND DISCUSSION

A. FTIR

The FT-IR spectra of the loaded and unloaded hydrogel is shown in Fig. *1* and Fig. *2* respectively.

Before adsorption of the dye the hydrogel shows a peak at 3331 cm^{-1}, which is related to -OH stretching. The peak at 1673 cm^{-1} are characteristics of carboxylate groups (asymmetric and symmetric) and the strong peak is for C=C groups. The peak detected at 1223 cm^{-1} refers to stretching vibration of the C-N groups. the peak at 922 cm^{-1}, can be ascribed to C=N and C-C stretching vibrations of the imidazole ring. The peak at 697 cm^{-1} refers to stretching vibrations of the C-N groups, the peak at 841 cm^{-1} refers to out of plane bending vibration of the C-H group in the imidazole ring and the peak at 1034 cm^{-1} refers to in-plane bending vibration of the C-H groups [37].

After adsorption a peak at 1580 cm^{-1} was observed which refers to the stretching vibration of C=C groups of a benzene ring and at 1343 cm^{-1} an aromatic tertiary amine appeared. At an adsorption peak of 1154 cm^{-1} C-H bending in the benzene ring appeared [37].

The adsorption peaks shifted after adsorption of the Brilliant Green dye.
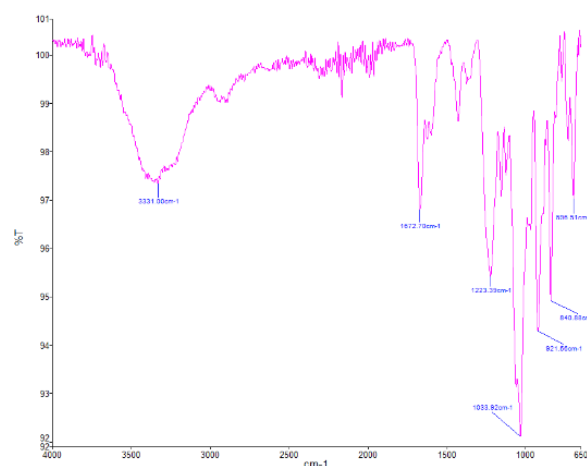

Fig. 1: FT-IR of loaded hydrogel

Fig. 2:FT-IR of unloaded hydrogel

B. Swelling of the hydrogel

The best swelling during hydrogel synthesis was experienced at a pH of 11, concentration of biopolymer (k-carrageenan) of 0.5 g, an initiator APS value of 0.02 g and 3 mL of the monomer acrylonitrile.

C. Adsorption study of BG dye: Effect of the adsorbent dose

Error! Reference source not found., displays the effect of the hydrogel dosage on the % dye removal. The maximum dye removal was 93 % at an adsorbent dosage of 50 mg and 70 mg. However, 40 mg was used further in the adsorption process, due to 40 mg having the optimum (92.5 %) dye removal efficiency. The % dye removal increases as the adsorbent dose increases, this is due to more surface area and active sites being present as the amount of the hydrogel increases. There was however not a major increase in % dye removal with the increase in hydrogel dose [37; 46].

D. Adsorption kinetics
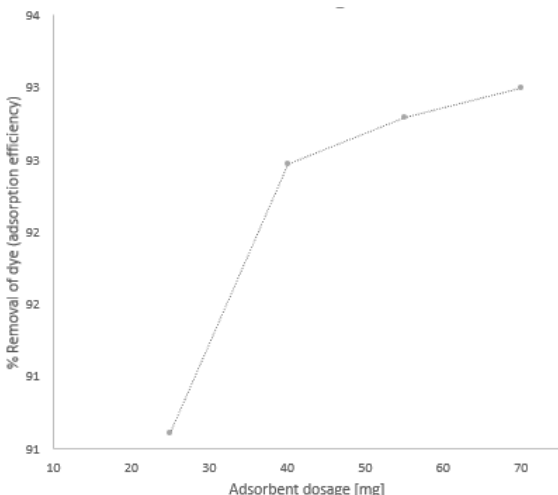

Fig. 3:Effect of adsorbent dose on adsorption

Kinetic models are established to determine the rate-controlling step of the adsorption process [24].

The pseudo-first order can be presented by Equation 4 and the pseudo-second order can be presented by Equation5.

$$\ln(q_e - q_t) = lnq_e - K_1 t \qquad (4)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

The amount of Brilliant Green adsorbed onto the adsorbent surface at time t (at equilibrium) is represented as $q_e \ and \ q_t$. The adsorption rate constants of the pseudo-first and second order are given as K_1 (1/min) and K_2 (g/mgmin).

The pseudo-first and second order were compared to one another and it was evident that the pseudo-second order, Fig. *5* , fit better to the experimental data ($R^2 = 0.956$) than the pseudo-first order ($R^2 = 0.252$), Fig. *4*. Implying the mechanism of adsorption is chemisorption [47-51].
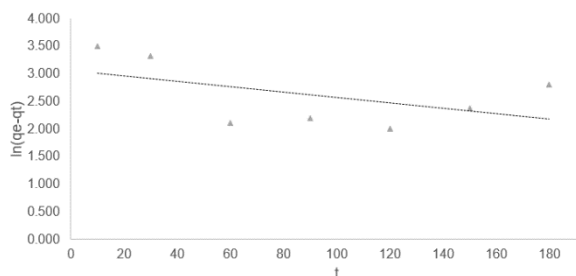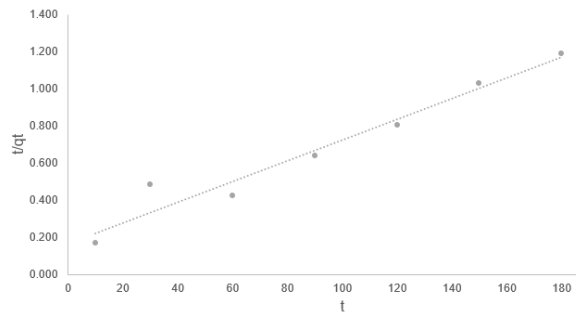

Fig. 4:Adsorption Kinetics-Pseudo-first order model

Fig. 5:Adsorption Kinetics-Pseudo-second order model

IV. CONCLUSION

The present work established that efficient removal of cationic dye (BG) on *k*-carrageenan –crosslinked poly (acrylonitrileco-acrylamide) hydrogel is possible. The optimum dosage for adsorption (dye removal) was observed to be 40 mg and considering the adsorption kinetics, the pseudo-second order fits the experimental data best.

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