Impact of Synthetic Clay as Filling Agents on the Dye Adsorption Capacity of Hydrogel

Elvis Fosso-Kankeu*, Frans Waanders, and Johannes Jacobus Venter

Abstract—The focus of this study was to investigate whether the adsorption capacity of a Kappa-carrageenan based hydrogel towards cationic dyes (Basic red and Brilliant green) could be increased by using synthetic clays, cloisite (C) as filling agents. Hydrogel-cloisite composites were synthesized by using a free radical graft co-polymerization technique. The hybrid nanocomposites were characterized using SEM and FT-IR spectroscopy. Adsorption experiments investigated the effects of the following parameters: adsorbent dosage, initial dye concentration, and contact time. The Langmuir- and Freundlich isotherm models were used to determine the hydrogel-cloisite nanocomposites adsorption affinity. The first- and second order kinetic models were used to determine the rate of adsorption of cationic dyes. It was found that using cloisite as filling agent for hydrogel resulted in improved adsorption capacity. The hydrogel-cloisite nanocomposite (H-C) displayed the best adsorption capacity for both dyes, with an equilibrium adsorption capacity of 64.14 mg/g for brilliant green (BG) dye and 58.73 mg/g for basic red (BR) dye. The nanocomposite saw a 20% improvement in adsorption capacity towards brilliant green dye and a 17% improvement towards basic red dye. Kappa-carrageenan hydrogel- clay composites can therefore be considered for the treatment of cationic dye containing wastewater.

Keywords—Cationic dyes; Adsorption; Hydrogel; Cloisite; Basic red; Brilliant green.

I. INTRODUCTION

Dyes are used in multiple industries to provide color to products from textiles to plastics. Some of these dyes are hazardous and need to be removed from industrial wastewater before it is discharged into the environment. They cause discoloration of water, leaving it aesthetically unpleasing. Colored water also has a negative impact on the environment as the dye could block certain wavelengths of sunlight which is crucial to the survival of aquatic life. [1 - 11] Dyes are relatively stable in water, which means that light, heat and oxidizing agents won't always remove or discolor the dye. [1] Thus a physical separation technique thus needs to be employed.

The main concern with dyes is that they could contain harmful substances like carcinogens and mutagens. [12] This

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would render the industrial waste water as toxic. This water thus has to be treated in order to correct the color and reduce the toxic effects. As clean water is becoming of ever growing importance there are numerous techniques available to treat industrial wastewater, each with their own limitations [13 - 17]. These techniques include: chemical degradation, adsorption, precipitation, biodegradation and chemical coagulation [18]. Biological methods require a lot of time and aren't very effective against synthetic polymer dyes. Chemical coagulation generates large amounts of sludge, which means it essentially trades one type of pollution for another. [19] Considers chemical degradation with chlorine to be highly effective, although it leads to the production of organochlorine compounds which are highly toxic. Ultrasonic and UV-ozone oxidation are also available, but not yet economically feasible [12]

Adsorption on the other hand is more favorable for water treatment since it is cost effective and has a small impact on the environment, especially when natural adsorbents like clays are used [20 - 25].

Hydrogel refers to a group of polymers in a three-dimensional network which is able to absorb large amounts of water (much like clay) without dissolving because they possess cross-linked polymer chains that are hydrophilic [26]. Hydrogels are used as adsorbents because they have certain functional groups (OH, NH_2, SO_3H, COOH, $COHN_2$) which are able to remove aqueous pollutants with electrostatic interactions [26]. Although hydrogel is effective at adsorbent there are still concerns with its stability and reusability. [27] Polysaccharide based hydrogels are low cost, biocompatible and biodegradable, which makes it the ideal candidate to use as adsorbent [28].

"Clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction of soils, sediments, rocks and water and may be composed of mixtures of fine grained clay minerals and clay sized crystals of other minerals such as quartz carbonate and metal oxides" [29 - 34]. Clays contain organized layered structures whereby they are grouped and they have a large water retention capacity. [29] Clay has the advantage of being a nanoparticle, this results in increased surface area and it increases the ability for surface ion exchange, which makes clay ideal for use in adsorption.[9] An approach that has shown improved adsorption capacities, is to enrich hydrogel polymers with clay to make a composite material. [20] The polymer composite material is expected to have much better adsorption capacities. Since the clay and hydrogel have similar properties that can be combined in order to complement each other [20].

In this study, the focus is to investigate the adsorption efficiency of a Polysaccharide based hydrogel when filled with synthetic clay.

II. EXPERIMENTAL

A. Materials

The following chemicals were used during experimentation: Acrylamide "AA" (Sigma Aldrich), N,N-Methylenebisacrylamide "MBA" (Sigma Aldrich), K-Carrageenan (Sigma Aldrich), Basic red cationic dye (Sigma Aldrich), Basic brilliant green cationic dye (Sigma Aldrich), Potassium persulfate "KPS" (Sigma Aldrich), Cloisite-20 was kindly offer by BYK-Chemie GmbH from Germany and Bentonite clay were obtained from the NWU School of Chemical and Minerals Engineering's storage facilities and had a particle size of 106 μm and smaller

B. Preparation of Hydrogel and Nanocomposites

The adsorbents were synthesized using a free-radical graft co-polymerization technique. 1 g of K-Carrageenan was added to 50 mL of deionized water in a 250-mL beaker and stirred with a magnetic bar for 10 minutes until completely mixed. 40 mg of KPs (initiator) was added to the solution and stirred for 5 minutes. Followed by the addition of 60 mg of MBA (Cross linker) and stirred for another 5 minutes. Finally, 1g AA (monomer) was added to the mixture and it was stirred again for 5 minutes.

The beaker was placed inside an incubator, at 45° C, to allow the reaction to continue for 24 hours.

The newly synthesized hydrogel was then allowed to cool to room temperature and cut into 5 mm by 5 mm cubes. The hydrogel cubes were submerged in deionized water in order to dissolve and remove homopolymer and unreacted monomers. The water was replaced every 24 hours for 7 days.
Finally, the hydrogel was dried in a hot air oven for 24 hours at 60 °C. The hydrogel was then crushed with a mortar and pestle and sieved to 106 micrometers.

For preparation of the Hydrogel-Cloisite nanocomposites, the aforementioned procedure was followed, with the exception that 2wt% cloisite was added to the mixture directly after adding K-Carrageenan.

C. Characterization of the Adsorbents

Characterization of the hydrogel(H), and hydrogel-cloisite nanocomposite(H-C) was done with an FT-IR spectrometer. Functional groups in the adsorbents were identified to evaluate the surface activation. The FT-IR spectrometry was done by using a IRAffinity-1S Fourier transform infrared spectrophotometer from Shimadzu with a spectral range from 4000-500 cm^{-1}.

D. Adsorption Studies

The equilibrium concentration of the dye solutions after adsorption was determined with a Genesys 10S UV-Vis spectrophotometer at the following optimal wavelengths: 426.5 nm for brilliant green dye and 290nm for the basic red dye.

Batch adsorption experimentation was carried out, the shaking incubator was set at a constant rotational speed of 160 rpm, the solution volume was kept constant at 0.1 L and temperature was kept at 25°C. The influence of the following parameters was investigated: adsorbent dosage (10-100 mg), contact time (10-145 min) and initial dye concentration (10-80 mg/L).

E. Isotherm and Kinetic Models

The adsorption affinity of H, H-C and H-B for the removal of brilliant green and basic red cationic dyes was evaluated by fitting Freundlich and Langmuir isotherms to the data. [35, 36]. The Langmuir isotherm model assumes that adsorption occurs in a monolayer about the adsorbent and is typically used with single solute systems. The linearized form of the Langmuir equation is given as follows: [37]

$$\frac{C_e}{q_e} = \frac{1}{k \cdot q_m} + \frac{C_e}{q_m} \tag{1}$$

The Freundlich model however, does not have any monolayer restrictions and can be applied to heterogeneous systems. The linearized form of the Freundlich equation is given as:[37]

$$\log q_e = \log k_f + \frac{1}{n} \cdot \log C_e \tag{2}$$

Where: C_e = the concentration of dye at equilibrium in[mg/L],
$\quad q_e$ = the equilibrium adsorption capacity in [mg/g]
$\quad q_m$ = Maximum adsorption capacity [mg/g]
$\quad$ k = the Langmuir constant related to energy released during adsorption [L/mg]
$\quad k_f$ = the Freundlich adsorption capacity parameter in (mg/g) and
$\quad$ n = the intensity of adsorption.

Pseudo first- and second order models were fitted to the adsorption rate data in order to assist with the determination of the adsorption rate [36]. The linearized pseudo first-order model is given by:

$$\log(q_e - q_t) = \log q_e - k_1 \cdot \frac{t}{2.303} \tag{3}$$

And the linearized pseudo second-order model is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t \tag{4}$$

where: q_e = the equilibrium adsorption capacity in [mg/g]
$\quad q_t$ = the adsorption capacity at time t in [mg/g],
$\quad k_1$ = the first order rate constant in [min^{-1}],
$\quad k_2$ = the second order rate constant in [g/mg.min^{-1}],
$\quad t$ = the time in [min].

III. RESULTS AND DISCUSSION

A. FT-IR Analyses

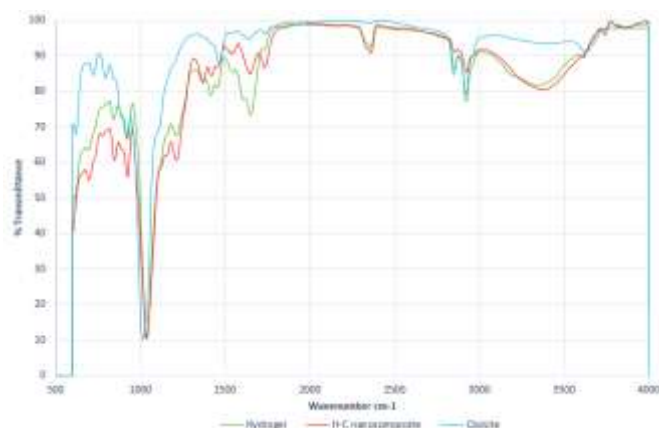The FT-IR results of the synthesized H, H-C composite and C before adsorption can be seen in Fig1.

Fig. 2: FT-IR spectra of (a) Hydrogel, (b) Cloisite and (c) H-C nanocomposite

From this figure it is evident that noticeable differences are present in the IR-spectra of H and H-C due to the cloisite influencing the structure of the hydrogel.

As is characteristic of kappa-carrageenan a strong adsorption band is present at about 843 cm^{-1}, which is due to C-O-SO$_3$ bond of D-galactose-4-sulphate (G4S). [29]

Another strong band is visible at approximately 928 cm^{-1} (between 925 and 935cm^{-1}) in the FTIR- spectra, which is characteristic of C-O bonds present in 3,6-anhydro-D-galactose (DA), another main constituent of Kappa-Carrageenan [29]

Another strong peak in adsorption occurs at 1038 cm^{-1} due to stretching vibration of its C-OH group and another absorption band at 1215 cm^{-1} indicates the presence of sulfate esters (S=O). The adsorption band at 1649 cm^{-1} is due to C=O stretch vibrations, indicating the presence of ketones of varying intensity in all three samples

The broad adsorption peaks between 3200 and 3600 cm^{-1} are due to stretching vibrations of the hydrogen bonded O-H and COOH-groups present in the hydrogel, cloisite and H-C composite. There is a 50 cm^{-1} shift rightwards in the adsorption band of the H-C composite when compared to the peak of H. The H-C peak also has a 3% increase in absorbance in this region, indicating that the cloisite filling altered the structure of the Hydrogel.

In the region 2915-2850 cm^{-1}, two strong peaks are present in the Hydrogel and cloisite samples, these peaks indicate a symmetric and asymmetric stretching vibration of (C-H) methyl groups that appear to have shifted upward and slightly to the right in the C-H composite. This is due to –CH$_3$ groups interposition in the two molecules

Increasing peak intensities in the region of 1450 and 1500 indicate the presence of secondary amine (N-H) bending vibrations in the H-C composite. Secondary amines are also present in pure hydrogel's structure, before filling with cloisite. However, there is a reduction in the intensity of these peaks, coupled with a leftwards shift confirm that the hydrogel was indeed modified.
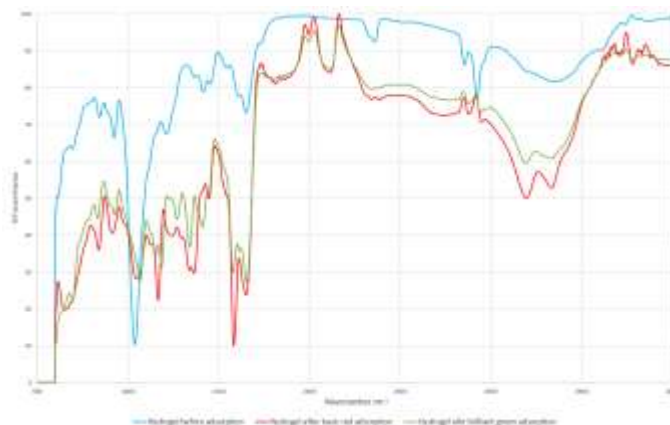

Fig. 3: FT-IR spectra of (a) Hydrogel and of Hydrogel after the adsorption of (b) BR and (c) BG

Fig. 3 illustrates the FT-IR spectra after basic red and brilliant green adsorption on pure hydrogel. It appears that hydrogel has a higher adsorption affinity towards the basic red dye, as the transmittance bands are experiencing taller peaks than those present in hydrogel after brilliant green adsorption, especially at the Ketone stretch region between 1625 and 1750 cm^{-1}. Hydrogel experienced a ketone stretch at 1700cm^{-1}, which was shifted left and substantially increased in intensity after dye adsorption. The asymmetric stretching vibrations of carboxyl (COOH) and hydroxyl (O-H) groups can be seen between 3200-3600 cm^{-1}. Another significant peak can be seen at 3250cm^{-1}, this peak isn't present in the pure hydrogel and is thus the result of hydrogen bonds between the dye and the hydrogel.

The H-C composites FT-IR spectra has almost the same peaks as the hydrogel after adsorption of dyes, with the main distinctions between them being the increase in the intensity of the adsorption bands found in H-C composite after dye adsorption. The clay filled hydrogel appears to have a greater adsorption affinity for the brilliant green dye.
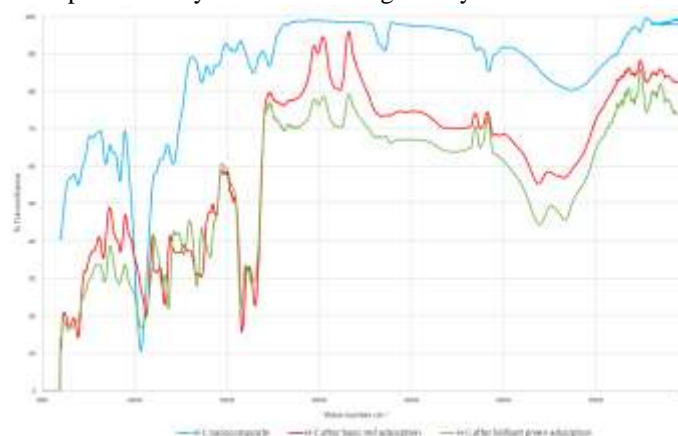

Fig.4: FT-IR spectra of (a) H-C nanocomposite and of H-nanocomposite after the adsorption of (b) BR and (c) BG

B. Adsorption Behavior

The effect of *adsorbent dosage* of Hydrogel and H-C composite is investigated in Fig. 5 below. The following

conditions were used: Initial dye concentration of dyes was kept constant at 50 mg/L, contact time was kept constant at 150 min, a temperature of 25°C was used and the mixture was stirred at 160rpm. Adsorbent dosages of 20, 40, 60, 80 and 100 mg were investigated. The optimum adsorbent dosage for BR and BG dyes was determined as 80 mg for all 3 adsorbents, and was used in further adsorption experiments. Too much or too little adsorbents resulted in fewer dye being removed. It was also observed that the hydrogel clay composites and the pure hydrogel appeared to favor the BG dye as it's removal efficiency was consistently the largest.
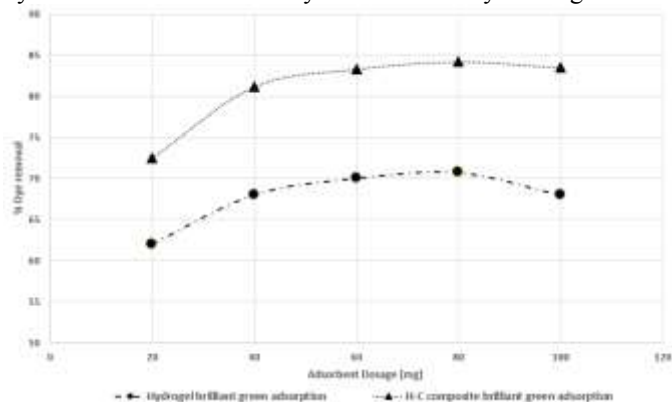

Fig. 5: Effect of adsorbent dosage on the adsorption of dye for a contact time of 150 min

The *optimum contact time* of the adsorption of cationic dyes, BR and BG, was determined to be 115 min for all 3 adsorbents. The adsorption experiments were done with the optimal absorbent dosage of 80 mg, an initial dye concentration of 50 mg/L investigated at the optimum adsorbent dosage and at a concentration of 50 mg/L. At a temperature of 25°C and a rotational speed of 160 rpm, it was found that the adsorption capacity of the adsorbent increased rapidly until 70 min and then increased slowly until it reached equilibrium at 115 min. This is due to the limited number of active sites available on the adsorbent. The H-C composite achieved the best adsorption capacity of 52.64 mg/g for BG vs the 44.19 mg/g achieved with Hydrogel.
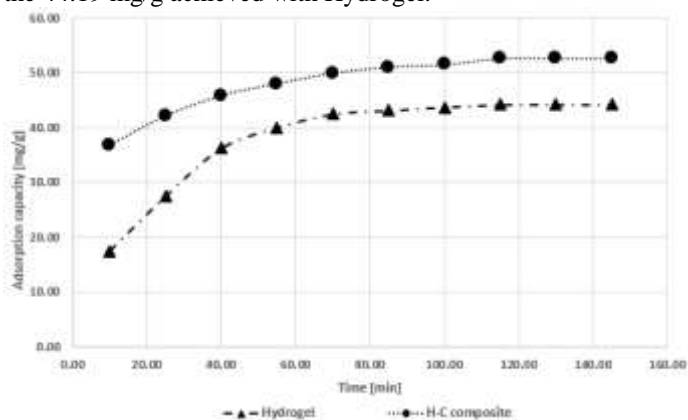

Fig 6: Effect of time on Brilliant green dye adsorption

The *optimal initial dye concentration*, as seen in Fig. 6, was determined at the optimal adsorbent dosage and contact time, while keeping temperature constant at 25°C and the shaking incubator at 160 rpm. Dye concentrations of 10, 20, 30, 40, 50,

60, 70 and 80 were investigated. Adsorption capacity of all 2 adsorbents increased rapidly until an initial dye concentration of approximately 60 mg/L was reached. After which the adsorption capacity seemed to decline slightly. The optimal initial dye concentration was determined as 60 mg/L for BG dye and 70 mg/L for BR dye. This could be due to the brilliant green dye having a larger adsorption affinity towards these adsorbents. Again the H-C composite achieved the best adsorption capacity at 65.15 mg/g and the pure hydrogel performed the worst with 53.05 mg/g.
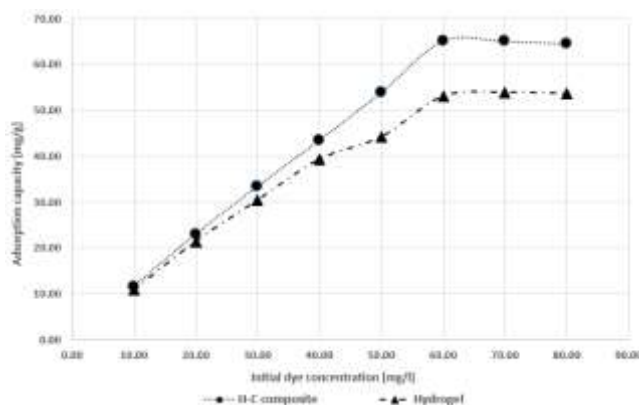

Fig 7: Effect of initial dye concentration on Brilliant green dye adsorption

C. Isotherm Model Results

A linearized Langmuir isotherm was plotted for the adsorption of BG dye by means of hydrogel and H-C composite (Fig.9). From the isotherms, trend lines were fitted and their coefficient of determination (R^2) was calculated, along with the constants of the Langmuir model. As the R^2 >0.98 the Langmuir model can be seen as a good fit for the collected data.
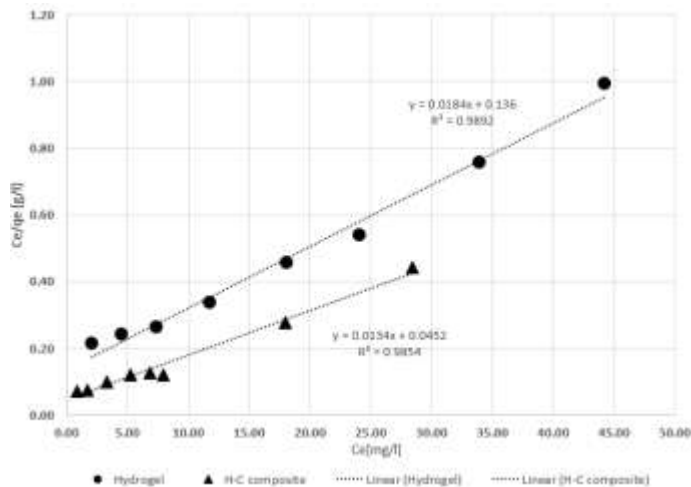

Fig 8: Linear regression of the Langmuir isotherm model

The Freundlich isotherm model was also fitted to the adsorption data, as can be seen in Fig.10. However, Table 1 shows that the calculated R^2 values are < 0.98, meaning the Freundlich model cannot be seen as the best fit for the adsorption data. The Langmuir model is therefore suitable to

predict the adsorption; implying that the BG dye is adsorbed onto the adsorbents by binding onto a monolayer surface.
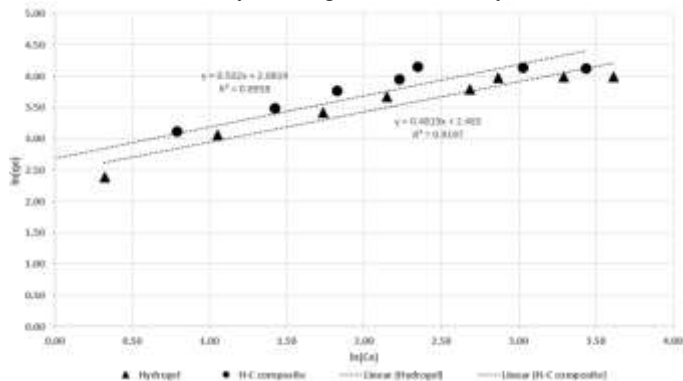

Fig. 9: Linear regression of the Freundlich isotherm mode

TABLE I
CONSTANTS FOR THE ISOTHERMAL

Models

	Langmuir isotherm		Freundlich isotherm	
	Hydrogel	H-C composite	Hydrogel	H-C composite
R^2	0.989	0.985	0.920	0.896
q_m [mg/g]	63.89	74.493	-	-
k [L/mg]	0.002	0.001	-	-
n	-	-	2.075	2.024
kf [mg/g]	-	-	11.763	14.613

Adsorption experimental data by plotting a graph of $\log(q_e - q_t)$ as a function of time (see Fig. 11). While for the pseudo second-order kinetic model, a graph of t/q_t as a function of time was plotted [38] (Fig.12). The calculated R^2 values and kinetic model constants can be seen in Table 2. The large R^2 values indicate that both kinetic models are good fits for the adsorption data in question [39]. With the pseudo second order kinetic model providing a slightly better fit to the data. Adsorption rate constants can be seen in Table II.
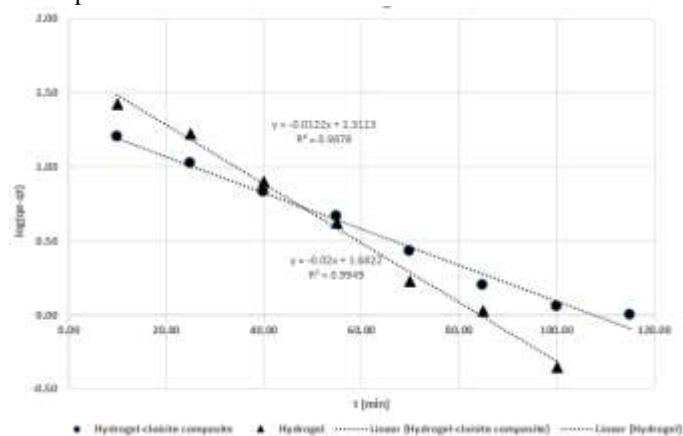

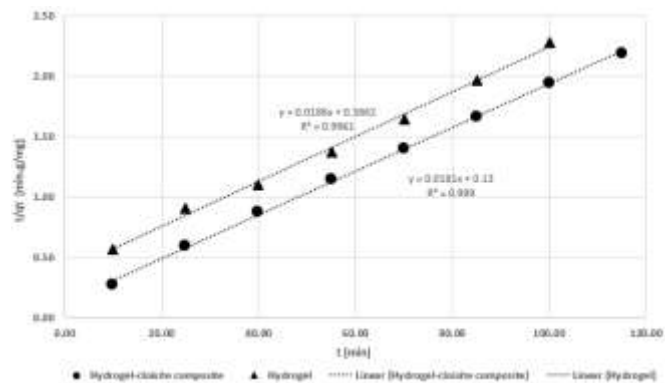Fig 11: Linear regression of pseudo first order kinetics

Fig 12: Linear regression of pseudo second order kinetic model

TABLE II CONSTANTS FOR THE PSEUDO FIRST- AND SECOND ORDER KINETIC MODELS

	Pseudo 1st order		Pseudo 2nd order	
	Hydrogel	H-C composite	Hydrogel	H-C composite
R^2	0.988	0.995	0.996	0.999
q_e [mg/g]	39.830	44.193	50.340	55.371
k_1 [min^{-1}]	0.027	0.022	-	-
k_2 [g/mg.min-1]	-	-	0.001	0.003

The R^2 values in Table II indicate that the experimental data can be represented by both the pseudo-first and pseudo-second order model as the R^2 values are both larger than 0.98. The modelled adsorption capacity of hydrogel and H-C composite are 50.34 mg/g and 55.37 mg/g as predicted by the pseudo-second order model (chemisorption mechanism) and 39.83 mg/g and 44.19 mg/g as predicted by the pseudo-first order model (physisorption mechanism), respectively, for brilliant green dye.

The results obtained in Table II clearly indicate that hydrogel and H-C composite are capable of quickly removing cationic dye from wastewater and that clay composites provide enhanced adsorption with synthetic clay offering the best improvements. This indicates successful synthesis of a hydrogel-clay nanocomposite. Similar results were obtained in previous studies [36, 38].

IV. CONCLUSION

From the characterization of adsorbents, it can be seen that hydrogel and H-C composite were synthesized successfully. From the adsorption experiments it can be concluded that using clay as a filling agent, delivers substantial improvements in the adsorbents adsorption capacity. The nanocomposite performed more than 20% better than the normal hydrogel. The results obtained throughout this study revealed that cloisite filled Hydrogel nanocomposite consistently showed superior adsorption capacities and affinity towards the BG cationic dye. The adsorption data were found to best fit the pseudo-second order kinetic model, implying that the adsorption of BG dye mainly occurred through a chemisorption mechanism. The filling of hydrogel with clay could therefore be considered as possible solution for the development of smart adsorbent for the removal of cationic dye from solution.

From the Isotherm data, the Langmuir model had the best fit, thus it can be concluded that most of the adsorption occurs on a single layer on the adsorbent material.

The batch kinetic studies revealed that the adsorption data corresponded excellently with pseudo first order and pseudo second-order kinetic models. Thus, both chemisorption and physisorption are taking place.

From the results obtained it can be concluded that hydrogel cloisite nanocomposite is the most effective adsorbent in the removal of BG and BR dyes from solution. It has an adsorption capacity of 64.14 mg/g for BG and 58.73 mg/g for BR. H-C composite can therefore be used for the removal of cationic dyes.

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