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Development of Hybrid Hydrogel Networks from Poly(Acrylamide-co-Acrylamido glycolic acid)/Cloisite Sodium for Adsorption of Methylene Blue

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ABSTRACT
Hybrid hydrogel networks synthesized by the simple free radical polymerization of acrylamide, acrylamidoglycolic acid and cloisite sodium clay. To synthesize these hybrid hydrogels N,N'-methylenebisacrylamide used as a cross linker and ammonium peroxydisulphate used as an initiator. The structural characterization of this poly(acrylamide-co-acrylamidoglycolic acid/cloisite hybrid hydrogels (PAAGC), were done using Fourier transform infrared spectroscopy. The resulting hybrid networks was used as an adsorbent for studying the effectiveness in the removal of methylene blue (MB), which is having a wide range of use in different fields such as biology and chemistry. The effects of contact time, initial sorbate concentration, pH, and dose of adsorbent were studied to optimize the adsorption capacity. The batch sorption technique employed, revealed a maximum adsorption. Adsorption isotherms and Kinetic models were fitted to know the adsorption mechanism. This Hybrid hydrogels exhibited excellent performance in MB adsorption. The investigations demonstrated that the PAAGC can be based as an efficient adsorbent for the removal of MB from aqueous solution.

Key words: *Acrylamidoglycolic acid, Cloisite clay, hybrid hydrogels, Methylene blue.*

1. INTRODUCTION

Most of the environmental problems have their solutions from the environment which are identified through research. Clays are among the cheapest, abundant, environmentally friendly, ion exchangeable adsorbents which can be used to substitute the expensive commercial activated carbon and also non-toxic when compare to pier which can substantially produce environmental pollution problems [1] Recent results have found simplest and effective methods with easy operational conditions for the treatment of aqueous textile effluents [2, 3]. In general the clays are either used in their natural state or by modification of clays by different processes such as calcinations, acid activation, pillaring, anion and cation exchange, organic modification with polymers or molecules and so on before usage [1].

In the past, various attempts have been made to develop effective treatment technologies for dye bearing wastewaters, but no single solution has been found to be satisfactory. Different physicochemical processes like adsorption, electro-kinetic coagulation, ion-exchange, membrane filtration, electrochemical oxidation, and photo-catalytic degradation processes have been attempted in treating these wastewaters [4]. Each technique has its own limitations such as generation of secondary effluent, hazardous intermediate products and slow rates of degradation. Thus, it is need of time to research into cleaner techniques for the effective removal of dyes from the effluent stream. Conventional treatment processes such as biological degradation, coagulation, chemical oxidation, ion exchange, and photo degradation are often unable to remove certain textile dyes from effluents because of its high solubility and low biodegradability [5]. However, adsorption has been recognized as a conventional process for the removal of dyes from effluents.

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Keeping all these in mind, authors synthesized the poly(acrylamide-co-acrylamidoglycolic acid)/ cloisite sodium nanocomposite hydrogels (PAAGC) for adsorption of Methylene Blue (MB) from aqueous solution. Swelling characteristics of PAAGC were performed in aqueous environment at ambient temperature. PAAGC characterized by Fourier transform infrared spectroscopy, X-ray diffraction and thermo gravimetric analysis. Removal of MB from aqueous solution has been achieved. The adsorption was studied as a function of contact time, adsorbent dose, pH, and temperature under batch adsorption technique. The equilibrium data fit with Langmuir, models of adsorption.

2. EXPERIMENTAL

2.1. Materials

Analytical Reagent grade samples of acrylamidoglycolic acid (AGA) purchased from Aldrich Chemicals Co. Ltd., USA, acrylamide (Am), Cloisite Clay, Methylene blue were purchased from Merck specialties Pvt. Ltd , Mumbai, India. Chemicals were used without further purification and double distilled (DD) water was used throughout the experiments.

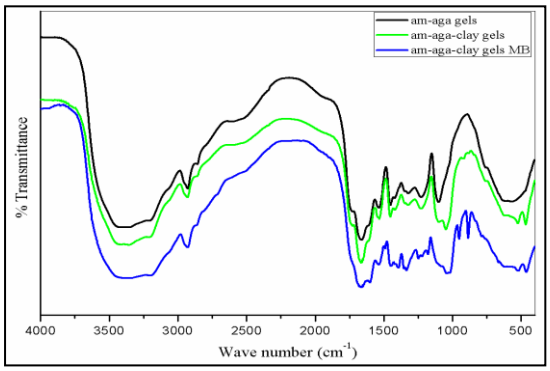

Figure 1: FTIR spectra of PAAGC hydrogels.

2.2. Preparation of Hybrid Hydrogels

PAAGC hydrogels were synthesized by employing free radical polymerization using N,N-methylene bis acrylamide (MBA) as a cross-linker and ammonium persulfate (APS) as free radical initiator. In detail, PAAGC hydrogels were prepared by first mixing (1 g) acrylamide (Am) 1.1417 g of acrylamidoglycolicacid (AGA) and 0.214g of Cloisite clay in 5 mL water. Another set of hydrogels were synthesized without clay. The hydrogels were removed, and kept in double distilled water (DD water) by changing DD water until all unreacted monomers removed from the gels, these gels were dried first at room temperature and finally in hot air oven. These dried gels were characterized by FTIR and XRD, studied swelling properties and dye adsorption studies.

3. RESULTS AND DISCUSSION

3.1. Characterisation

Fourier transform infrared spectroscopy (FTIR) spectral measurements of pure hydrogels, PAAGC hydrogels and methylene blue loaded PAAGC hydrogels were performed using Perkin Elmer (model spectrum two, England (UK)) spectrophotometer. The PAAGC hydrogels were finely grounded with KBr to prepare the pellets under a hydraulic pressure of 600 dynes/m^2 and spectra were scanned between 4000 to 400 cm^{-1}. FTIR spectra of PAAGC are reported in Figure1. The strong peak around 3449 cm^{-1} due to the stretching vibration of -OH or NH_2 group, peaks at 1658, 1673 cm^{-1} belongs to amide (C=O, N-H) stretching and 1612 cm^{-1} and 1390 cm^{-1} belongs to COOH asymmetric and symmetric stretching, in addition, the bands around 1310 cm^{-1}, 1160 cm^{-1}, 1090 cm^{-1}, 990 cm^{-1} and 2900 cm^{-1} are attributed to polymer skeleton (C-O, C-C, -CH stretching and bending vibrations) of PAAGC hydrogels. In clay gels FTIR spectrum in addition to above distinctive peaks at 3450 and 950 cm^{-1} which represents Si-OH stretching vibrations. The peaks at 1080, 800, 561 and 455 cm^{-1} belong to Si-O-Si, Si-O and O-Si-O vibrations respectively. Where as in methylene blue adsorbed hydrogels significant change is observed in amide, carboxylic and silicate bands shows MB is chemisorbed into the PAAGC hydrogels.

XRD of PAAGC is reported in Figure 2. The XRD pattern of PAAGC hydrogels shows characteristic diffraction peak at 2θ value of 6.4° corresponding to 001 plane with d spacing of 13.6 A° [6]. Pristine hydrogels shows a broad peak at 2θ value 20° and PAAGC shows peaks at 2θ value 6.0° and 20°.

3.2. Static Adsorption Studies

The adsorption studies of the MB on the PAAGC hydrogels were carried out by batch experiments studies. To the test solutions, added PAAGC hydrogels and kept for equilibrium time. Finally, the resulted solution was used for determining its methylene blue content by UV-visible Spectrophotometry. Optical photographs of ppm solutions of methylene blue before and after adsorption with PAAGC hydrogels is presented in figure 3.

3.3. Effect of pH

The effect of pH on adsorption capacity was conducted by mixing 0.02 gm PAAGC adsorbents with 30 mL of 400 ppm aqueous solution with different pH value ranging from 3-10 static condition for 24 h water bath, and then the residual MB concentrations were determined. The effect of pH on adsorption of MB on PAAGC hydrogels is shown in figure 3.

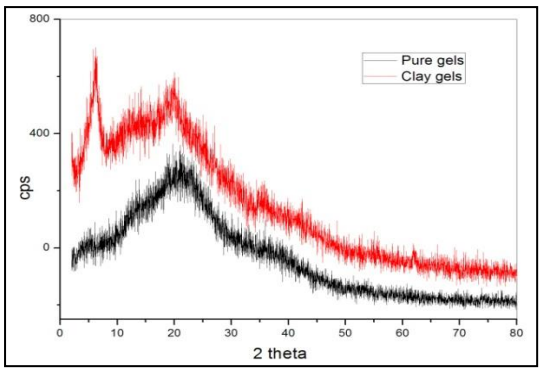

Figure .2: XRD of PAAGC hydrogels.

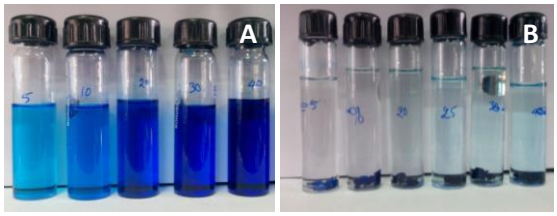

Figure 3: Optical photograph of ppm solutions of methylene blue before (A) and after (B) adsorption with PAAGC hydrogels.

3.4. Adsorption Kinetics

Adsorption dynamics is used to describe the solute uptake rate which controls the residence time of adsorbate to uptake the molecules at the solid-solution interface. The effect of time on equilibrium adsorption of PAAGC hydrogels is reported in figure (5a). Two kinetics models were used to analyze adsorption kinetics, namely, pseudo-first order, pseudo-secondorder. The pseudo first-order, pseudo-second order models are presented by the following equations.

$$\log(C_e - Q_t) = \log C_e - \frac{K_1}{2.303}\, t \qquad (4)$$

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

The kinetic parameters for adsorption of methylene blue by PAAGC based hydrogels are given in graphs are shown in figure: (5b&5c). Based on the obtained correlation coefficients (r^2),

3.5. Effect of Adsorbate Concentration.

The isotherms were linearised by several batch experiments PAAGC hydrogel were equilibrated with varying initial concentrations of MB at pH 6.0. After equilibrium time 24 hours the hydrogels were removed from the solutions and the solutions were analysed by UV-visible spectrophotometer for residual amount of MB.

Langmuir isotherm is given by the equation (6). And its linearized form is given in equation (7)

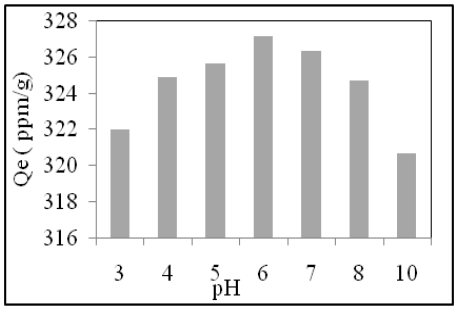

Figure 4: Effect of pH on equilibrium adsorption of PAAGC hydrogels

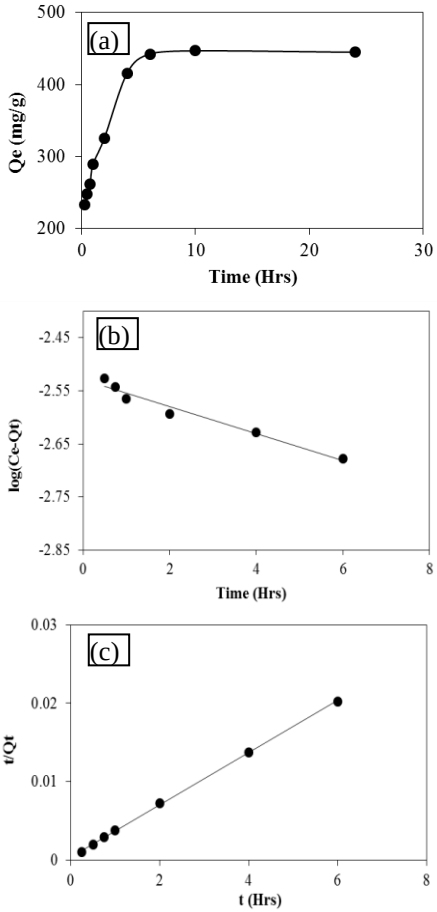

Figure.5: (a) Effect of time on equilibrium adsorption (b) first order kinetics (c) second order kinetics of PAAGC hydrogels.

where Q is the amount of adsorbed methylene blue on the PAAGC based hydrogels at equilibrium ($mg.g^{-1}$), Ce is the equilibrium concentration of methylene blue in solution (ppm) and Qmax and b are Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively.

$$Q = \frac{Q_{max}\, b\, C_e}{1 + b\, C_e} \qquad (6)$$

$$\frac{Ce}{Q} = \frac{1}{Q_{max}} C_e + \frac{1}{b\, Q_{max}} \qquad (7)$$

The Freundlich isotherm modeles based on the assumption of adsorption on heterogeneous surfaces and possibly in multilayer adsorption and is usually given as

$$Q = K_F Ce^{1/n} \quad (8)$$

Where K_F and n are the Freundlich constants related to adsorption affinity and adsorption intensity, respectively. The Freundlich equation can be linearised in logarithmic form for the determination of Freundlich constants as:

$$\log Q = \frac{1}{n}\log C_e + \log K_F \quad (9)$$

4. CONCLUSION

Synthesized PAAGC hydrogels. Characterized with FTIR, based on FTIR studies hydrogel structure is predicted. The peaks in the metal loaded gel IR spectra shows that metal ions are bound to hydrogels. Swelling studies and methylene blue adsorption studies performed; maximum adsorption achieved is 560 mg/g of PAAGC hydrogels.

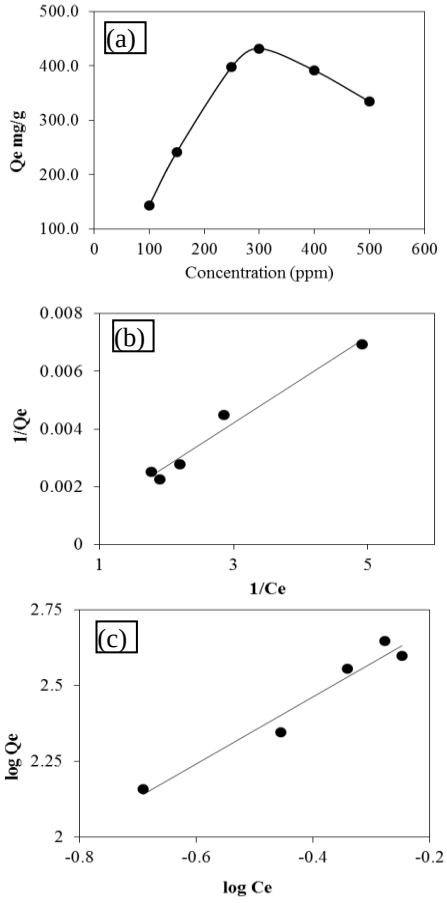

Figure.5:(a) Effect of concentration on equilibrium adsorption (b) long muir isotherm (c) freundlich isotherm of PAAGC hydrogels

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Langmuir isotherm constants			
	K_L	**Q_{max}**	**R^2**
	$3.53x10^8$	530 mg/g	0.972
Freundlich isotherm constants			
	K_f	**n**	**r^2**
	812.83	0.9	0.955

Table 1: Isotherm model constants for adsorption of MB by PAAGC hydrogels.

5. REFERENCES

[1] M. Auta, B.H. Hameed, (2012) Modified mesoporous clay adsorbent for adsorption isotherm and kinetics of methylene blue, ***Chemical Engineering Journal 198-199***, 219-227.

[2] A. Xue, S. Zhou, Y. Zhao, X. Lu, P. Han (2010) Adsorption of reactive dyes from aqueous solution by silylated palygorskite, ***Applied Clay Science***, ***48***, 638-640.

[3] V. Vimonsesa, B. Jina, C.W.K. Chow, C. Saint, (2010) Development of a pilot fluidized bed reactor system with a formulated clay–lime mixture for continuous removal of chemical pollutants from wastewater, ***Chemical Engineering Journal, 158,*** 535–541.

[4] S. R. Shirsath, A. P. Patil, R. Patil, J. B. Naik, P. R. Gogate, S. H. Sonawane, (2013) Removal of Brilliant green from wastewater using conventional and ultrasonically prepared Poly(acrylic acid) hydrogel loaded with Kaolin clay: A comparative study, ***Ultrasonics Sonochemistry***, ***20***, (3) 914-923.

[5] V. Janaki, K. Vijayaraghavan, A.K. Ramasamy, Kui-Jae Lee, Byung-Taek Oh, Seralathan Kamala-Kannan, (2012) Competitive adsorption of Reactive Orange 16 and Reactive Brilliant Blue R on polyaniline/bacterial extracellular polysaccharides composite-A novel eco-friendly polymer, ***Journal of Hazardous Materials***, ***241- 242,*** 110- 117.

[6] Seema Monika Datta, (2013), Clay–polymer nanocomposites as a novel drug carrier: Synthesis, characterization and controlled release study of Propranolol Hydrochloride, ***Applied Clay Science***, ***80-81***, 85-92.