



Preparation, Characterization and Application of $Mg(OH)_2$ -PAM Inorganic-Organic Composite Polymer in Removing Reactive Dye

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Abstract: In this study, a series of inorganic-organic composite polymer was prepared. Magnesium hydroxide and polyacrylamide was composed in a composite matrix to prepare $Mg(OH)_2$ -PAM (MHPAM) inorganic-organic composite polymer. The characteristics of MHPAM inorganic-organic composite polymer was investigated in terms of chemical, physical, physical, thermal and morphological properties through FT-IR, conductivity, intrinsic viscosity, TGA and TEM, respectively. Results showed that the properties of MHPAM composite polymers varied with the compositions in the composite polymers. Different compositions of MHPAM inorganic-organic composite polymers were applied in removing reactive dye from aqueous solution. MHPAM inorganic-organic composite polymer with $Mg(OH)_2$: PAM ratio of 90 : 10 gave the best dye removal (%) where it was able to remove 98% of reactive dye at pH 11.00 with a dosage of 500 mg/L. Kinetics study was carried out using different dye concentration and it was found that the experimental data fitted the pseudo-second-order model better compared to pseudo-first-order model.

Key words: Inorganic-organic composite polymer; Magnesium hydroxide; Polyacrylamide, Reactive dye.

INTRODUCTION

Textile industry is one of the industries that poses a high demand on water supply and produces large amounts of wastewater. Reactive dye is one of the common dyestuffs used in the textile industry to colour cellulosic and cotton-based fabric. The degree of fixation of dye is never complete during the dyeing process and this result in producing coloured effluents. As such, the wastewater from textile industry is often characterized with high pH, alkalinity and temperature, contains high concentration of organic matter, non-biodegradable matter, toxic substances, detergents, soaps, oil, grease, sulfide and suspended/dissolved solids [1]. This highly polluted wastewater is highly toxic to the organics and cause skin irritation, cancer, and mutation of aquatic organic organisms and humans [2]. Therefore, the wastewater from the textile industry needs to be treated before being discharged into the environment or municipal treatment plant.

To address the problem of textile industrial wastewater, rapid development and technological innovation have been initiated to develop novel materials for wastewater treatment. Inorganic-based coagulants and organic-based flocculants which have been extensively using are not able to fulfill all technological requirements for wastewater treatment [3]. Researchers discovered that the mixtures of

materials to produce hybrid materials show superior performance compared to their respective original components. Thus, effective substances have been incorporated into secondary matrixes to form new hybrid materials to improve the performance of wastewater treatment due the synergetic effect of two components in one material [4, 5]. There are several groups of hybrid materials have been produced for wastewater treatment and they can be generally classified into three primary groups, such as structurally-hybridized materials (composite), chemically-bound-hybridized materials and functionally-hybridized materials [6]. Structurally-hybridized material refers to the hybridization of macroscopic structures where combination of different materials takes place in a single matrix. Such a hybrid materials are also known as composites [7, 8]. For chemically-bound-hybridized materials, a new chemical group is introduced into the molecule of materials to produce a new hybrid complex [6]. Chemically-bound-hybridized material can be produced through chemical modification, e.g. copolymerization, chemical grafting and so forth. Combination of two different functional materials into one matrix refers functionally-hybridized materials. Such a combination of two functional materials in one matrix requires only one unit operation instead of the conventional two-stage of processes, i.e. coagulation and flocculation [7, 8].

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Such innovation is essential in reducing the wastewater treatment processing time especially for those industries that are dealing with large volume of wastewater, especially textile industry.

In this study, MHPAM inorganic-organic composite polymer was prepared using magnesium hydroxide and polyacrylamide. The characteristics of MHPAM inorganic-organic composite polymer were investigated in terms of chemical, physical, thermal and morphological properties. MHPAM inorganic-organic composite polymer was applied in removing reactive dye from aqueous solution. The treatment performance was determined based on the percentage removal of reactive dye from synthetic dyeing wastewater containing Cibacron Red FN-R. The kinetics of the dye removal using MHPAM inorganic-organic composite polymer was carried out to determine the rate of reactive dye removal at different initial dye concentration.

MATERIALS AND METHODS

Materials: Acrylamide (AM) (>99% purity, Merck) was used without further purification. Ammonium persulphate (AR, System) and sodium bisulfite (GR, Acros Organics) were used as redox initiators. Magnesium hydroxide (95–100%, System) was used as received. Deionized water was used in the preparation of inorganic-organic composite polymer.

Preparation of inorganic-organic composite polymer: To prepare MHPAM inorganic-organic composite polymer, magnesium hydroxide was premixed in aqueous solution with polyacrylamide with certain composition as described in our previous paper [9]. Prior to any application, MHPAM inorganic-organic composite polymer was aged for 24 hours at room temperature prior to any application.

Characterization of inorganic-organic composite polymer

Fourier Transform Infrared (FT-IR) analysis: An Avatar 360 FT-IR spectrophotometer was used to determine the chemical composition and functional groups of MHPAM inorganic-organic composite polymer. MHPAM inorganic-organic composite polymer was dried through solvent-casting prior to be prepared into pellet with potassium bromide. FT-IR was operated with a resolution of 4 cm⁻¹ and scanning range from 4000 to 400 cm⁻¹. The MHPAM inorganic-organic composite polymer contained pellet was tested after completion of the blank spectrum scanning.

Conductivity of inorganic-organic composite polymer in aqueous solution: A conductivity meter (HACH, Sension5) was used to measure ionic content of the MHPAM inorganic-organic composite polymer in aqueous solution at different concentration.

Intrinsic viscosity measurement: Intrinsic viscosity is an approximation method to estimate the average molecular weight and it is directly related to the bridging capacity of the composite polymer. The viscosity of MHPAM

inorganic-organic composite polymer in aqueous solution was measured using Ubbelohde viscometer and Density meter (Anton Paar, DMA 38) at 30°C. Viscosity of MHPAM inorganic-organic composite polymer in aqueous solution was determined by:

$$\eta = A\rho t \quad (1)$$

where η = solution viscosity, A = calibration constant of the viscometer, ρ = density of the aqueous solution, and t = flow time.

Specific viscosity of MHPAM inorganic-organic composite polymer in aqueous solution was determined by:

$$\eta_{sp} = \frac{\eta_c - \eta_0}{\eta_0} \quad (2)$$

A linear regression was fitted using reduced viscosity (nsp/C) versus concentration. The intrinsic viscosity was determined at c = 0 of the fitted linear regression

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (3)$$

where $[\eta]$ = intrinsic viscosity, η_{sp} = specific viscosity, C = concentration of aqueous solution of MHPAM inorganic-organic composite polymer, η_1 = viscosity of aqueous solution of MHPAM inorganic-organic composite polymer, η_0 = viscosity of water.

Thermal gravimetric analysis: The thermal gravimetric analysis was carried out using TGA (Perkin Elmer, Pyris 1). The weight of an empty platinum pan was measured prior to any measurements to obtain zero weight of the sample. The dried solvent-casted MHPAM inorganic-organic composite polymer sample was loaded into the platinum pan. The reaction was initiated by immersing the sample-loaded pan in a heating furnace and heat was supplied at rate of 10°C/min. The sample was heated from temperature 35 to 800°C. The thermal decomposition was recorded in a differential thermal gravimetric curve.

Transmission electron microscopy (TEM): The morphology of MHPAM inorganic-organic composite polymer in aqueous solution was analyzed by TEM (Philips, CM12). One drop of MHPAM inorganic-organic composite polymer in aqueous solution was carefully placed on the copper grid and dried with a filter paper. The sample-coated copper grid was then put under TEM for image viewing.

Removal of reactive dye from aqueous solution: HPAM inorganic-organic composite was used in removing reactive dye (Cibacron Red FN-R, CI Reactive Red 238, C₂₉H₁₅O₁₃S₄ClFN₇Na₄, molecular weight: 944.2 g/mol) from aqueous solution. Synthetic reactive dye wastewater was prepared with a concentration of 250 mg/L. The pH of the reactive dye aqueous solution was adjusted using acid and base. The flocculation was carried out using a high torque stirrer (IKA LABORTECHNIK RW20DZM.n). MHPAM inorganic-organic composite

polymer was introduced into the reactive dye aqueous solution and agitation speed of 100 rpm was applied for 5 minutes. After allowing sedimentation of 30 minutes, the dye residual that remained in the supernatant was measured with spectrophotometer (HACH DR2800) at $\lambda_{\max} = 540$ nm.

RESULTS AND DISCUSSION

Characterization of inorganic-organic composite polymer: The properties of inorganic-organic composite polymer vary with the chemical component and composition. The performance of the composite polymer in wastewater treatment is controlled by the key properties of chemical, physical, thermal as well as morphological characteristics. Thus, the properties of the inorganic-organic composite polymer should be investigated prior to applying the composite polymer in dye wastewater treatment.

Chemical properties: The compositions and functional groups of inorganic-organic composite polymer are determined by FT-IR spectrophotometer. The corresponding FT-IR spectra for the functional groups of inorganic-organic composite polymer are shown in Fig. 1. In the spectra, $3696.36\text{--}3695.54\text{ cm}^{-1}$ is observed for $-\text{OH}$ (dilute solution) for MHPAM inorganic-organic composite polymer. The sharp singlet peak of hydroxyl ($-\text{OH}$) group becomes prominent with the increase of magnesium hydroxide ratio in the MHPAM inorganic-organic composite polymer. Primary amines $-\text{NH}_2$ (NH stretch), primary amides $-\text{CONH}_2$ (NH_2 deformation and $\text{C}=\text{O}$ stretch), alkyl $\text{R}-(\text{CH}_2)$ deformation) and amides ($\text{C}-\text{C}=\text{O}$) are observed at wavenumbers $3460.63\text{--}3434.61\text{ cm}^{-1}$, $1670.22\text{--}1648.71\text{ cm}^{-1}$, $1457.72\text{--}1456.09\text{ cm}^{-1}$ and $462.32\text{--}460.65\text{ cm}^{-1}$, respectively. The presence of methylene ($-\text{CH}_2$) group is observed at $2925\text{--}2850\text{ cm}^{-1}$. However, the intensity of the peak decreases gradually with the increase of $\text{Mg}(\text{OH})_2$ ratio in MHPAM inorganic-organic composite polymer. It is noted that no new chemical bond is formed when magnesium salts is premixed with polyacrylamide, which reveals that magnesium salt-polyacrylamide is a physical mixture. However, hydrogen bonding could be formed between magnesium hydroxide and electronegative nitrogen atom of polyacrylamide [9].

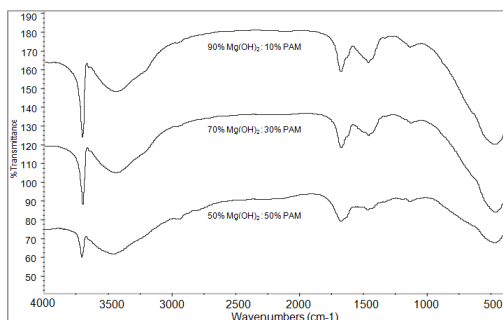


Fig. 1: FT-IR spectra for MHPAM inorganic-organic composite polymer

Physical properties: For the physical properties of inorganic-organic composite polymer, conductivity and intrinsic viscosity are taken into account. The conductivity of MHPAM inorganic-organic composite polymer in aqueous solution at different concentrations is shown in Fig. 2. The conductivity is used to determine the ionic content of composite polymer when it is introduced into the aqueous solution. The conductivity increases with the ratio of magnesium hydroxide ratio in MHPAM inorganic-organic composite polymer. A linear relationship is observed between the conductivity of MHPAM inorganic-organic composite polymer in aqueous solution at different concentrations which is in agreement with our previous study [9]. At the same concentrations, reduced viscosity was measured to determine intrinsic viscosity for MHPAM inorganic-organic composite polymers. Fig. 3 shows the reduced viscosity of different ratios of MHPAM inorganic-organic composite polymers at different concentrations. An inverse behaviour is observed for reduced viscosity compared to conductivity. The intrinsic viscosity increases from 50 to 258 mL/g with the ratio of polyacrylamide.

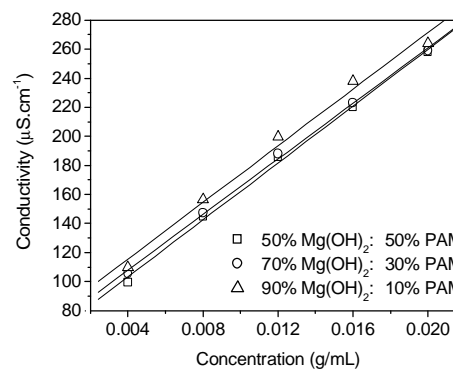


Fig. 2: Conductivity of MHPAM inorganic-organic composite polymer in aqueous solution at different concentrations

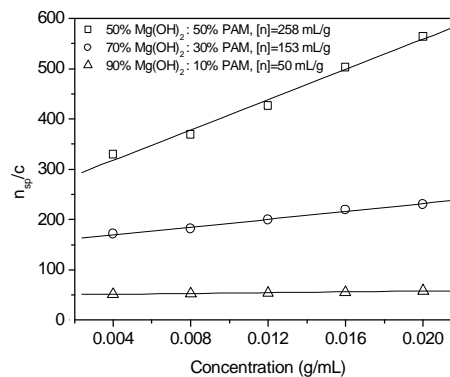


Fig. 3: Reduced viscosity of MHPAM inorganic-organic composite polymer at different concentrations

Thermal properties: Thermal properties of inorganic-organic composite are investigated through TGA. The thermal decomposition of MHPAM inorganic-organic composite polymer is shown in Fig. 4 in the form of thermal gravimetric curves. With the increase of magnesium hydroxide ratio, the thermal stability is enhanced. This is could be attributed to the hydrogen bonding network formed between the electronegative nitrogen atom of polyacrylamide with magnesium hydroxide [10]. From the differential thermal gravimetric curve in Fig. 5, it is noted that there are three stages of thermal decomposition. The first thermal decomposition stage of MHPAM inorganic-organic composite polymer is observed in the range of 35–205°C, followed by the second stage at 205–290°C. The third thermal decomposition stage occurs beyond 300°C; where MHPAM composite polymers are decomposed completely at about 450°C. The thermal gravimetric curves stay unchanged beyond 450°C and the weightlessness is due to the total thermal decomposition of polyacrylamide backbone in MHPAM inorganic-organic composite polymers [10].

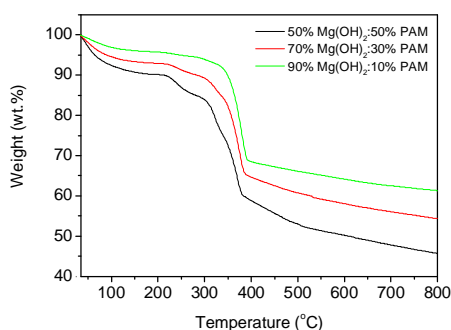


Fig. 4: Thermal gravimetric curves of MHPAM inorganic-organic composite polymers

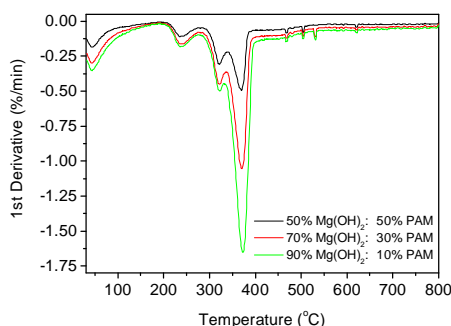


Fig. 5: Differential thermal gravimetric curve of MHPAM inorganic-organic composite polymers

Morphological properties: The morphological properties of MHPAM inorganic-organic composite polymer in aqueous solution was investigated by TEM. The microstructure of MHPAM inorganic-organic

composite polymer is shown in Fig. 6. It is noted that magnesium hydroxide particles are absorbed onto the chain of polyacrylamide. It could be due to hydrogen bonding that is formed between magnesium hydroxide and electronegative nitrogen atom of polyacrylamide [9].

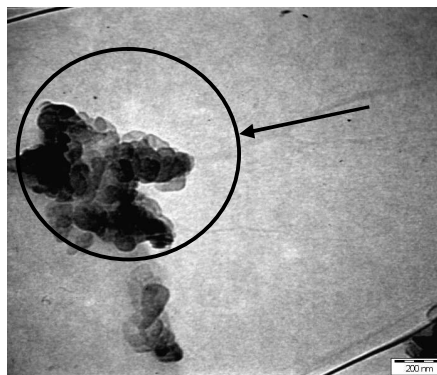
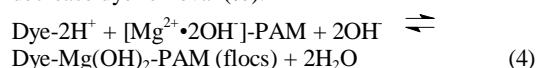


Fig. 6: TEM image of MHPAM inorganic-organic composite polymer in aqueous solution.

Removal of reactive dye using inorganic-organic composite polymer

Effect of pH: Reactive dyes are designed initially for cellulosic fiber dyeing. It is usually applied to a fiber in a basic dye bath and forms a chemical bond with the fiber. However, reactive dye can also be used to dye wool and nylon in which they are applied under acidic condition. In this study, MHPAM inorganic-organic composite polymer was applied to remove reactive dye in acidic condition (pH was fixed at 2.00). Magnesium hydroxide from MHPAM inorganic-organic composite polymer is able to neutralize the acidic condition as well as remove reactive dye from aqueous solution through flocculation. The effect of pH is shown in Fig. 7. The result shows that MHPAM inorganic-organic composite polymer work well at pH 11.00 in removing reactive dye from acidic aqueous solution. MHPAM inorganic-organic composite polymer with the ratio of Mg(OH)₂:PAM (90 : 10) gives the highest dye removal (%) of 98%. However, the dye removal (%) decreases with the decrease of the ratio of magnesium hydroxide. The mechanism of dye removal is proposed in Equation 4. MHPAM inorganic-organic composite polymer is dissociated into [Mg²⁺•2OH⁻]-PAM when it is introduced into the acidic aqueous solution of reactive dye. To reach pH 11.00, addition of OH⁻ is needed to bind with dye molecule and [Mg²⁺•2OH⁻]-PAM to form Dye-Mg(OH)₂-PAM (flocs) and releasing H₂O into the supernatant. Such a mechanism causes the pH to drop to near neutral pH with the release of H₂O. Excess of OH⁻ ions (beyond pH 11.00) cause the forming of precipitable species which in turn results in the decrease dye removal (%).



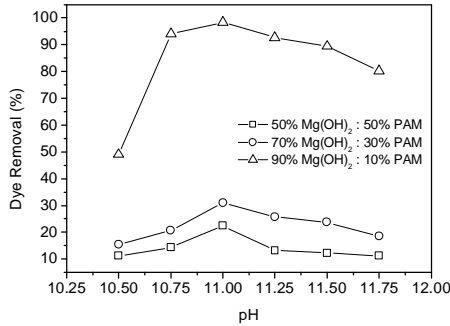


Fig. 7: Effect of pH on dye removal (%) using MHPAM inorganic-organic composite polymers

Effect of dosage: As shown in Fig. 8, MHPAM inorganic-organic composite polymer with the ratio of Mg(OH)₂:PAM (90 : 10) was selected in removing reactive dye from acidic aqueous solution with different dosages. The maximum dye removal (%) is achieved at a dosage of 500 mg/L but the dye removal (%) decrease thereafter. Such an observation is due to reactive dye requiring only a certain dosage of MHPAM inorganic-organic composite polymer for binding to form flocs. Further increase of dosage causes the re-suspension of flocculated dye into the supernatant.

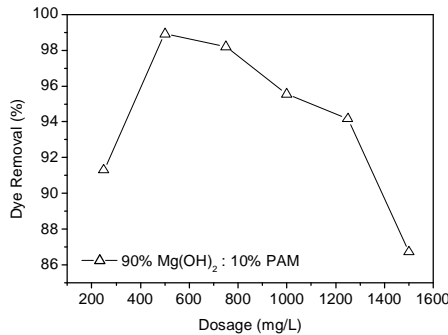


Fig. 8: Effect of dosage on the dye removal using MHPAM inorganic-organic composite polymer

Kinetics of dye removal: To investigate the kinetics of dye removal, the rate constants of dye removal with respect to different initial dye concentrations are described by pseudo-kinetics model [11]. The dye removal rate is represented by:

$$\frac{dC}{dt} = -kC^n \tag{5}$$

where C = concentration of dye, n = order of interaction between dye and hybrid material, k = rate constant, t = operating time.

To fit a pseudo-first order reaction model,

$$\ln\left(\frac{C_t}{C_o}\right) = -k_1 t \tag{6}$$

A linear plot using $\ln\left(\frac{C_t}{C_o}\right)$ versus t is constructed

in which the slope of the plot gives the value of the rate constant, k₁ (1/min).

where C_o = initial dye concentration, C_t = concentrations at time, t = time (min).

To fit a pseudo-second order reaction model,

$$\frac{1}{C_t} - \frac{1}{C_o} = k_2 t \tag{7}$$

A linear plot using $\left(\frac{1}{C_t} - \frac{1}{C_o}\right)$ versus t is constructed

in which the slope of the plot gives the value of the rate constant, k₂ (L/(mg.min)).

where C_o = initial dye concentration, C_t = concentrations at time, t = time (min).

The rate constants of both kinetics models are calculated by fitting linear regression using pseudo-first order model and pseudo-second order model. Table 1 show the rate constants and their R² value for MHPAM composite polymer in removing dye at different initial dye concentrations. Results show that the kinetics data of dye removal using MHPAM composite polymer fits pseudo-second order model better than pseudo-first order model where R² value for pseudo-second order model is higher than that of pseudo-first order model. The rate constant of dye removal decreases from 0.0225 to 0.0008 L/mg.min) with the increase of initial dye concentration from 100 to 250 mg/L. The rate constant of the dye removal is strongly depending on the initial dye concentration where the rate constants decrease with the initial dye concentration. This is due to the decrease in activity of dye molecules as the dye molecule has consumed the MHPAM composite polymer during the process of interaction among themselves [11].

Table 1: Kinetics rate constants with pseudo-first order and pseudo-second order models for dye removal using MHPAM at different initial dye concentrations

Initial dye concentration (mg/L)	Pseudo-first order model		Pseudo-second order model	
	k ₁ (1/min)	R ²	k ₂ (L/mg.min)	R ²
100	0.3609	0.9219	0.0225	0.9510*
150	0.1369	0.8046	0.0093	0.8087*
200	0.0779	0.9684	0.0032	0.9704*
250	0.0585	0.9090	0.0008	0.9143*

CONCLUSIONS

MHPAM inorganic-organic composite polymer was prepared using magnesium hydroxide and polyacrylamide. The characteristics of MHPAM inorganic-organic composite polymer were investigated in terms of chemical, physical, thermal and morphological properties. FT-IR shows that MHPAM inorganic-organic composite polymer is a physical mixture considering that there is no new chemical bonding formed. The conductivity of MHPAM inorganic-organic composite polymer in aqueous solution increases with the ratio of magnesium hydroxide ratio. However, the intrinsic viscosity behaves inversely where it decreases with the increase of magnesium hydroxide ratio. For thermal properties, the thermal stability is enhanced with the increase of magnesium hydroxide ratio in MHPAM inorganic-organic composite polymer. It is observed from TEM viewing, that magnesium hydroxide particle was absorbed onto the chain of polyacrylamide. This could be due to the formation of hydrogen bond between magnesium hydroxide and electronegative nitrogen atom of polyacrylamide. The results show that MHPAM inorganic-organic composite polymer gives the best dye removal of 98% at pH 11.00 and dosage of 500 mg/L. Kinetics study has been carried out at different dye concentration using MHPAM inorganic-organic composite polymer and the results showed that experimental data fitted pseudo-second-order model better compared to pseudo-first-order model with their relatively higher R^2 value.

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support from Universiti Sains Malaysia in the form of postgraduate fellowship as well as Research University grant (RU 1001/PTEKIND/814049) which have resulted in this paper.

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