

Research Article

Adsorption of Malachite Green Dye from Liquid Phase Using Hydrophilic Thiourea-Modified Poly(acrylonitrile-co-acrylic acid): Kinetic and Isotherm Studies

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Thiourea-modified poly(acrylonitrile-co-acrylic acid) (TU-poly(AN-co-AA)) adsorbent was a surface modification of poly(acrylonitrile-co-acrylic acid) synthesized by facile redox polymerization. Surface functionalization with thiourea was carried out to provide hydrophilicity on the surface of a polymeric adsorbent. Fourier transform infrared (FTIR) spectrometer, scanning electron microscope (SEM), and Zetasizer characterized the morphology and structures of TU-poly(AN-co-AA). Copolymerization of poly(acrylonitrile-co-acrylic acid) and its successful incorporation of the thioamide group was confirmed by the FTIR spectra. The SEM micrographs depicted uniform and porous surface morphologies of polymeric particles. The average diameter of modified and unmodified poly(acrylonitrile-co-acrylic acid) was 289 nm and 279 nm, respectively. Zeta potentials of TU-poly(AN-co-AA) revealed the negatively charged surface of the prepared polymer. Adsorption capacities of hydrophilic TU-poly(AN-co-AA) were investigated using malachite green (MG) as an adsorbate by varying experimental conditions (pH, initial concentration, and temperature). Results showed that the pseudo-second-order reaction model best described the adsorption process with chemisorption being the rate-limiting step. Furthermore, Elovich and intraparticle diffusions play a significant role in adsorption kinetics. The equilibrium isotherm has its fitness in the following order: Freundlich model > Temkin model > Langmuir model. Thermodynamic analysis indicates that the sorption process is spontaneous and exothermic in nature. The reusability results suggested potential applications of the TU-poly(AN-co-AA) polymer in adsorption and separation of cationic malachite green dye from wastewater.

1. Introduction

The treatment of dye bearing industrial wastewater is a global environmental challenge faced by government agencies and scientific community. This is due to adverse effects on environment and human beings [1, 2]. Presence of dyes in waterbodies pollute natural habitat and constitute health problems because they are not biodegradable and complex by nature [3, 4]. Malachite green (MG) dye is not only used in textile, paper, rubber, and leather industries for product colouring but equally used as antiprotozoan,

fungicide in fishery, and medical disinfectant. Research however showed that MG is harmful to freshwater animals in acute and chronic exposure [5]. It is highly toxic to mammalian cells and organs like liver, kidney, lung, spleen, and skin [6, 7]. Therefore, it is imperative to eliminate dyestuff from coloured wastewater for environmental safety and health benefits.

Adsorption [8], photocatalytic degradation [9], biodegradation [10], and chemical oxidation [11] are developed physical and chemical treatment/purification methods to remove dye from wastewater. Adsorption stands out

amongst all treatment technologies as the most effective for adsorption of dye due to its design flexibility, relatively low cost, adaptation to broad range of dyes, and simple operation [12, 13]. However, sludge generation, poor selectivity, long contact time, poor site accessibility, and nonrecyclability of adsorbents are limitation to adsorption application. Therefore, it is required to prepare functional adsorbents with reasonable cost, efficiency, and regeneration ability.

Recently, chemical modification of reactive functional groups for creation of different new or additional functionalities has become attention-grabbing art in material science and engineering field. Design of materials with desired specified formulation and morphology is made possible with this modification technology [14]. With this development, polymeric materials containing amine, amide, thioamide, or amidoxime groups that cannot be synthesized directly by polymerization can now be easily produced by postpolymerization modification. These functionalized or modified polymers possess complexing capacity with various organic pollutants especially synthetic dyes and other pollutants in liquid phase environment [15, 16]. Its application is not limited to wastewater treatment but catalysis, biomedical, and others [17, 18].

Acrylonitrile (AN), as the high carbon source material, can be polymerized with monomers like methyl acrylate, acrylic acid, vinylbenzyl chloride, and itaconic acid for indirect synthesis of polymers with thio-functionalities [19–21]. Different shapes (spherical), fibres, and hydrogel polymers can be prepared by AN copolymerization. Once hydrophobic nitrile groups containing polymer is prepared, dipole of nitrile groups can be modified into thioamide groups via postpolymerization. Nitrile groups can also be converted to amidoxime, amine, hydrazine, amidrazone, and carboxyl groups by the above similar chemical modification route [18, 19, 21–23]. For instance, Kampalananwat and Supaphol report the modification of polyacrylonitrile (PAN) with NaOH ethanolic solution for metal ion adsorption, although it is a costly and complicated process [24]. Goscianska et al. produced an ordered mesoporous carbon material, functionalized with amine group and applied as an adsorbent to remove solophenyl red 3BL (SR) [25]. Bayramoglu et al. synthesized magnetic beads containing aminated fibrous surfaces for sorption of reactive green 19 dye from aqueous solution [26]. Sheng et al. prepared polyacrylonitrile (PAN), functionalized with thio to enhance its adsorptive properties. Faghihi and Hazendonk also described the postpolymerization modification of vinylbenzyl chloride (VBC, 15 mol%) and methyl methacrylate (MMA, 85 mol%) with thiuronium [27]. Postsurface modification of poly(vinylbenzyl chloride) beads with the amidoxime group for high sorption of organic dyes and heavy metals was reported by Ajmal et al. [15].

The potential of modified polymeric materials as the adsorbent largely depends on various reactions that can be performed on the inorganic surface and expanded chain on the modifying agent. Thiourea is chosen among functional groups due to its high content of nitrogen and sulphur as electron donor atoms [28–30] and its capacity to attach to the pendant polymer chain [31]. Herein, new hydrophilic

thiourea-modified poly(acrylonitrile-co-acrylic acid) denoted as TU-poly(AN-co-AA) was prepared by redox polymerization of acrylonitrile (AN) and acrylic acid (AA) and functionalized with thiourea. Thioamide groups on polymer chains act as binding sites for the positively charged dye molecules. The characterization, adsorption kinetics, and adsorption isotherms studies of prepared adsorbents on the MG adsorbate were investigated.

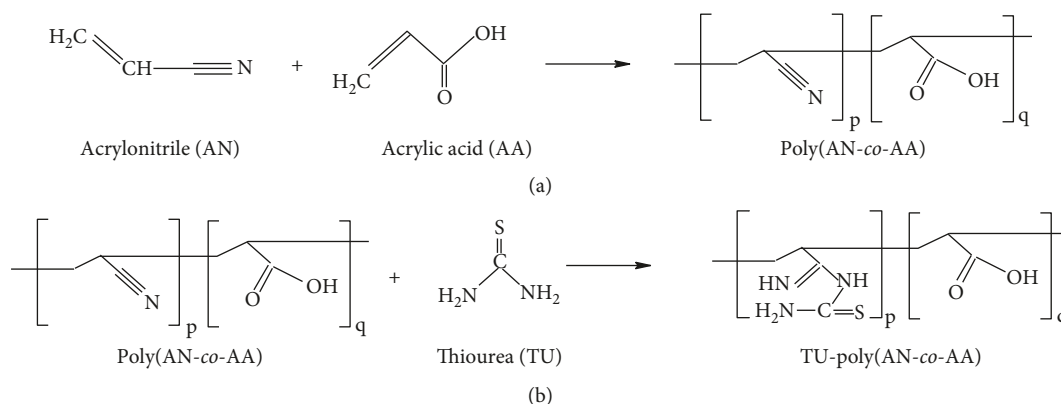
2. Materials and Methods

2.1. Chemicals. Acrylonitrile (AN) and acrylic acid (AA) (monomers) were taken from Acros Organics, New Jersey, USA, and purified by passing through an alumina column. Sodium bisulphate (SBS) and potassium persulphate (KPS) (initiators) and thiourea (TU) were purchased from R&M Chemicals, Essex, UK. Ethanol and methanol were purchased from System ChemAR, Shah Alam, Malaysia. Malachite green (MG) dye (from Acros Organics, New Jersey, USA) was used as the adsorbate. All chemical reagents were of analytical grade.

2.2. Synthesis and Modification of Poly(acrylonitrile-co-acrylic acid). Redox polymerization of acrylonitrile- (AN-) 97.0% and acrylic acid- (AA-) 3.0% was performed at 60°C under nitrogen gas in a three-necked round bottom flask, fitted with a water condenser. The reaction medium, deionized water (200 mL), was initially purge with nitrogen gas at 40°C for 30 minutes. Then, 2.09 g of SBS and 2.16 g of KPS were added to the reaction medium followed by 0.275 mol of AN and 0.029 mol of AA. The solution was mechanically stirred at 200 rpm using an egg-shaped magnetic stirrer. The free radical polymerization reaction was allowed for 2 hours. The poly(AN-co-AA) polymer formed was precipitated in methanol for an hour and then successfully washed with methanol and deionized water. The polymer was oven-dried in *vacuo* at 45°C until constant weight is obtained. It is a modified technique employed by Zahri et al. [20].

The surface of the synthesized polymer, poly(AN-co-AA), was modified with thiourea to produced hydrophilic thiourea-modified poly(AN-co-AA). The modification process was as follows: 6.0 g of TU and ethanol-water mixture (1/2 vol.%) were stirred at 200 rpm for 30 minutes at a constant temperature of 50°C. Then, 5.0 g of poly(AN-co-AA) was added to the solution at 100°C for 5 hours. The resulting crystal TU-poly(AN-co-AA) was rinsed in ethanol deionized water solution, filtered, and dried to constant weight at 50°C. The overall preparation and modification process is illustrated in Scheme 1.

2.3. Preparation of Aqueous Dye Solutions. Malachite green (MG) (Scheme 2) dye of a commercial grade and purity was used without purification. The dye stock solution of concentration of 1000 mg/L was prepared by dissolving 1.0 g of dye in distilled water. The experimental solutions of different initial concentrations ranging from 20 to 100 mg/L were obtained by diluting the MG dye stock solution.



SCHEME 1: Polymerization of poly(AN-co-AA) (a) and modification of poly(AN-co-AA) with thiourea (b).



SCHEME 2: Physical and chemical structures of malachite green (MG).

2.4. Characterization of the Modified and Unmodified Poly(AN-co-AA)

2.4.1. FTIR Analysis. The modified and unmodified poly(AN-co-AA) were analysed to detect the functional groups present in it using Fourier transform infrared spectrophotometer (PerkinElmer, 1750X-PerkinElmer Inc., Waltham, MA, USA). The region of the infrared was between 4000 and 500 cm^{-1} at room temperature.

2.4.2. SEM Images. The morphology of modified and unmodified poly(AN-co-AA) samples were obtained using the scanning electron microscope (SEM) (Hitachi S-3400N High-Technologies Corporation, Minato, Tokyo, Japan) and operated at 10 to 20 kV. Samples were coated in Au film prior to analysis. The diameters and particle size distributions were measured using ImageJ™ software (version 1.52a) from SEM image analysis of 100 individual particles

2.4.3. Zeta Potential. Zeta potential provides essential information about surface charges of the adsorbent for rapid understanding of interaction between the adsorbate and the adsorbent. Zetasizer Nano Series (Malvern Panalytical Limited, United Kingdom) was used to measure the surface charge(s) of synthesized and chemically modified polymers.

2.5. Batch Adsorption Experiments. Adsorptive tests of MG dye on thiourea-modified poly(AN-co-AA) in the batch system was studied/performed using 250 mL volumetric flasks. 100 mL dye solutions (MG) at varying concentrations (20 to 100 mg/L) were prepared, and a known amount (g) of TU-poly(AN-co-AA) was mixed with solution for single dye adsorption tests. Under constant stirring speed of 100 rpm, the solutions were controlled at 25°C and 100 rpm agitation speed. At the varying time interval, 10 ml solution was withdrawn and filtered and supernatant dye concentration was measured by Lambda 35 UV-Vis spectrophotometer at 617 nm maximum wavelength. The dye removal percentage, R , was calculated using equation (1) and adsorption capacity at the equilibrium (q_e) condition using equation (2):

$$\%R = \frac{C_0 - C_e}{C_0} \times 100, \quad (1)$$

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

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of the cationic dye (mg/L), respectively; q_e is the amount of the adsorbed dye (mg/g); V is the volume of the solution (L); and m is the weight of the TU-poly(AN-co-AA) adsorbent used (g).

Classical approach was adopted to investigate the effect of various key process parameters: adsorbent dose, reaction time, initial concentration, temperature, and pH, on the removal of MG.

2.6. Adsorption Kinetics. Adsorption kinetics studies were carried out in 250 mL flasks containing 100 mL of MG dye solution with a known quantity of the TU-poly(AN-co-AA) adsorbent. The volumetric flasks were agitated for time intervals between 0 and 120 minutes on a water bath shaker at 100 rpm at room temperature (25°C). The samples were taken at varied time interval and filtered, and supernatant dye concentration was analysed. The data obtained were analysed using pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, and intraparticle diffusion (IPD) kinetic models.

2.7. Adsorption Equilibrium. Adsorption equilibrium investigation was performed also in 250 mL flasks containing 100 mL of MG dye solution of different initial concentrations (20 to 100 mg/L) with a known amount of adsorbents. The mixture was constantly agitated in a water bath shaker at 100 rpm at 25°C for 1 hour. The equilibrium concentration was determined and analysed using various isotherm models such as Langmuir, Freundlich, and Temkin adsorption isotherm models.

2.8. Adsorption Thermodynamics. Adsorption of MG cationic dye was investigated at various temperatures ranging from 298 to 328 K in the water bath shaker at 100 rpm agitation speed for 60 minutes. The enthalpy changes (ΔH^0), entropy changes (ΔS^0), and Gibbs free energy changes (ΔG^0) were thermodynamic parameters employed to determine the nature and spontaneity of the adsorption process.

3. Results and Discussion

3.1. Characterization of Poly(AN-co-AA) and TU-Poly(AN-co-AA). FTIR technique was used to analyse and identify the functional groups present in synthesized poly(AN-co-AA) and evaluate postmodification changes in chemical structures. FTIR spectra and absorption bands of the two samples were recorded in the range of 4000–500 cm^{-1} as shown in Figure 1. The characteristic peaks at 1725 cm^{-1} and 2932 cm^{-1} correspond to the bonds -C=O and -CH, respectively. The broad band at 2244 cm^{-1} and 3516 cm^{-1} , respectively, represents -C \equiv N (nitrile group) and -OH (hydroxyl group) of the poly(AN-co-AA) copolymer [19, 20, 33]. After thiourea modification, some of the functional group(s) in poly(AN-co-AA) diminished or increased and disappeared, and formation of new functional groups was observed. The disappearance of the peak at 2244 cm^{-1} , shift of bands at 3516 cm^{-1} to 3345 cm^{-1} , and appearance of bands at 1614 cm^{-1} (-C=N) and 729 cm^{-1} (-C=S) confirmed successful incorporation of thioamide to the polymer surface according to report of Zahri et al. [20].

The scanning electron microscope (SEM) micrographs of the raw poly(AN-co-AA) and TU-poly(AN-co-AA) polymers are shown in Figure 2. The morphologies of both were similar to each other, and the surface of the TU-poly(AN-co-AA) polymer shows no significant cracks or degradation signal. They have almost uniform spherical morphology and porous surface suitable for adsorption

binding sites. The SEM photos of modified and unmodified synthesized polymers depicted the spherical beads agglomerated morphologies due to intraparticle bonds existed between monomers, solution low viscosity, and complex polymerization reaction nature [34–37]. The average particle size of TU-poly(AN-co-AA) slightly increased from 279 nm to 289 nm, and this increment in average particle size of the polymer beads is an evidence that the thioamide group has been successfully incorporated to the nitrile group of synthesized poly(AN-co-AA). Similar trend of increase in particle size was also observed and reported in [19, 20, 34, 38].

Zeta potentials of poly(AN-co-AA) (P) and TU-poly(AN-co-AA) (MP) samples at a varied pH value were negative both in acidic and alkaline conditions (Figure 3). The aqueous dispersion of TU-poly(AN-co-AA) was also found negative in the neutral pH, emanated from the low negative value of zeta potential (-3.4 mV). These negative surface charges confirmed the availability of negatively charged functional groups at the edges of the modified polymer surface since thioamide, carbonyl, and hydroxyl groups leads to extreme hydrophilicity with negative charge density [39–41].

3.2. Dye Adsorption Application of Poly(AN-co-AA) and TU-Poly(AN-co-AA). Malachite green dye adsorption potentials of synthesized poly(AN-co-AA) and TU-poly(AN-co-AA) were studied in the batch system. The effect of thiourea modification on MG dye adsorptive performance of prepared polymer samples is presented in Table 1. The adsorption capacity of poly(AN-co-AA) (at an varied dosage) is low as observed from Table 1. The surface of the unmodified polymer contains only -COOH groups which permit only hydrogen bonding interaction with a hydrogen donor site of the MG molecules [14].

After modification with thiourea, decoration of pendant thioamide groups on the polymer surface culminated to creation of more negatively charged surfaces. Then, adsorption capacity was improved significantly at 0.5 g dosage by 20.81% for sorption of MG, compared with the adsorption capacity of the nonmodified sample. In this evaluation, the thiourea ligand creates a multianionic centre for interaction with cationic MG molecules and enhanced the sorption capacity. Henceforth, the modified poly(AN-co-AA) adsorbent was selected for a detailed study of the MG dye adsorption process.

3.3. Effect of Adsorbent Dosage. The doses of TU-poly(AN-co-AA) varied from 0.3 to 1.2 g/100 mL. Figure 4 revealed that percentage of MG removal sharply increased with increase in the amount of the adsorbent from 0.3 to 0.5 g/100 mL and then reached almost a constant value. This is attributed to the availability of more adsorbent binding sites and adsorptive surface area [42–44]. No significant improvement in the MG removal percentage was observed as dosage increased beyond 0.5 g to 1.2 g/100 mL; hence, 0.5 g of adsorbent dose was selected for successive studies as the optimal load of TU-poly(AN-co-AA).

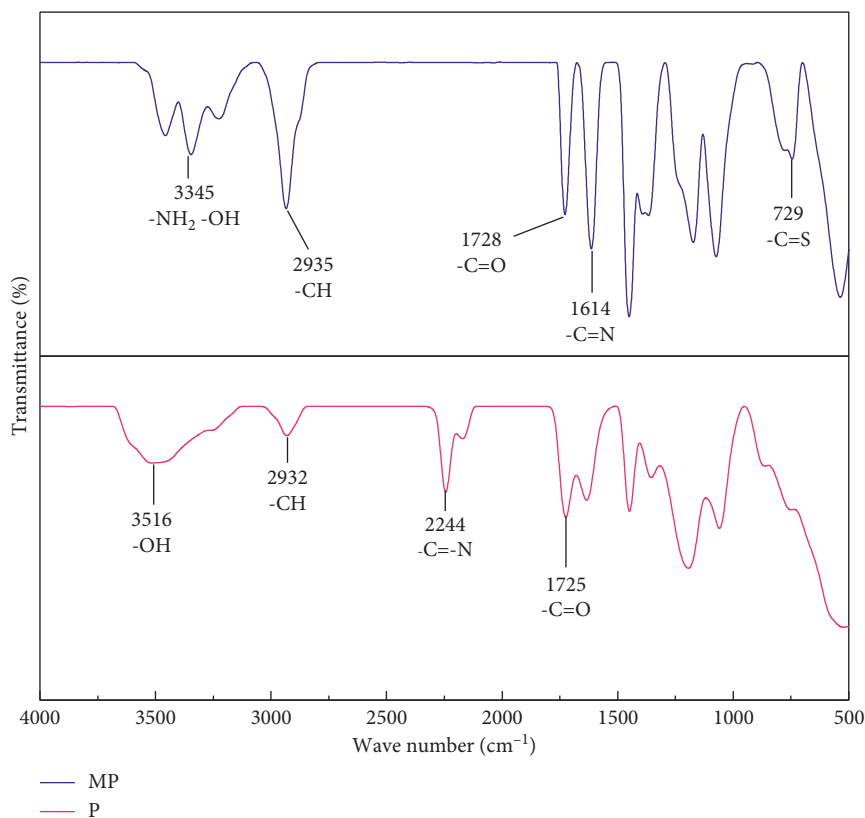


FIGURE 1: FTIR spectra of poly(AN-co-AA) (P) and TU-poly(AN-co-AA) (MP) polymers.

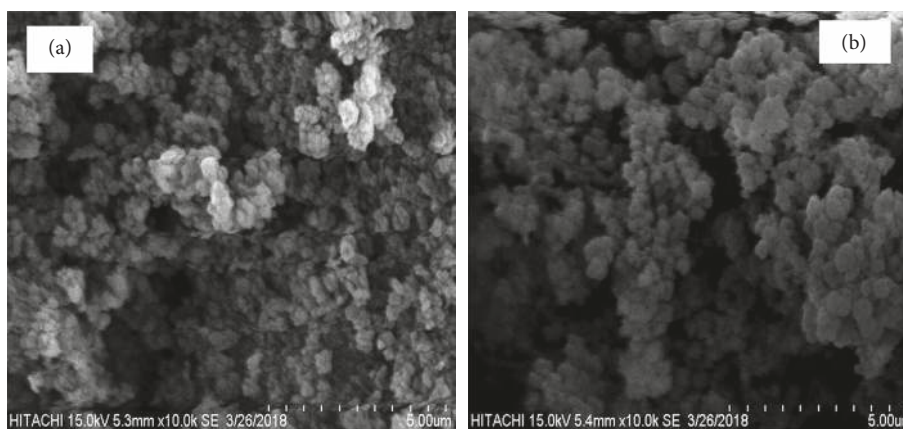


FIGURE 2: SEM micrographs of poly(AN-co-AA) (a) and TU-poly(AN-co-AA) (b).

3.4. Effect of Contact Time and Initial MG Concentration.

The adsorption of MG molecules on the surface of adsorbents is a time-dependent process. Hence, the time necessary for sorption of MG was optimized in order to evaluate the TU-poly(AN-co-AA) polymer's utilization period. The time dependency of the adsorption of MG onto TU-poly(AN-co-AA) was investigated for different dye concentrations over the range of 20 to 100 mg/L, and the results obtained are presented in Figure 5. The adsorption experiments were carried out for a contact time up to 120 minutes. The time-dependent adsorption of MG dye indicates that 60 minutes of contact time

was required for most of the sorption of dye molecules to reach equilibrium. The results revealed that quantity of MG removal increases fast as the initial concentration increases. This may be attributed to the increase in driving force induced by a concentration gradient from high initial solution concentration and availability of maximum active sites.

It was observed that over 60% of the MG removal occurred in the first 30 minutes and subsequently increases till the 60 min contact time, where maximum treatment ensued. Beyond 60 min till 120 min as the treatment time, dye removal was constant which can be ascribed to the equilibrium

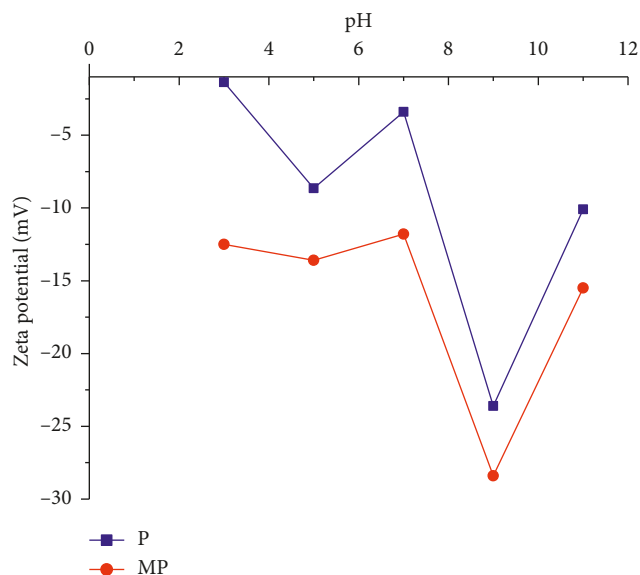


FIGURE 3: Zeta potentials of poly(AN-co-AA) (P) and TU-poly(AN-co-AA) (MP) under different pH values.

TABLE 1: Adsorption test of poly(AN-co-AA) and TU-poly(AN-co-AA).

Adsorbent	Dosage (g)	Extent of removal (%)	Improvement (%)
Poly (AN-co-AA)	0.3	53.07	—
	0.5	65.44	—
	1.0	68.30	—
TU-poly (AN-co-AA)	0.3	64.88	11.81
	0.5	86.25	20.81
	1.0	89.98	21.68

MG concentration: 80 mg/L; agitation speed: 100 rpm; temperature: $25 \pm 2^\circ\text{C}$; contact time: 2 hrs.

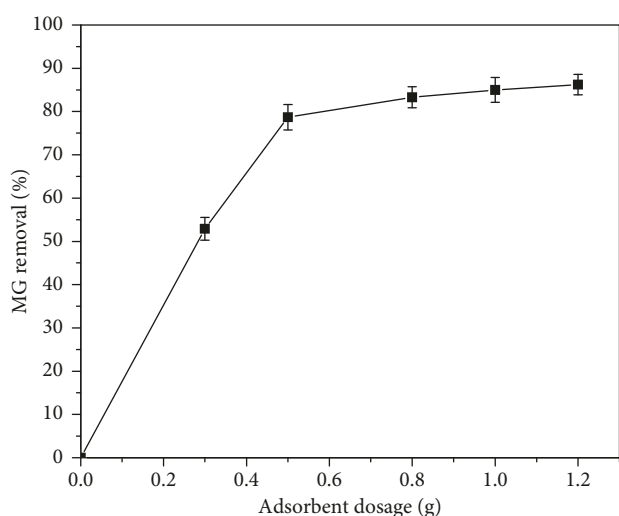


FIGURE 4: Effect of adsorbent dosage on the adsorption of MG onto TU-poly(AN-co-AA) (concentration: 50 mg/L; temperature: 298 K; contact time: 60 min; agitation speed: 100 rpm).

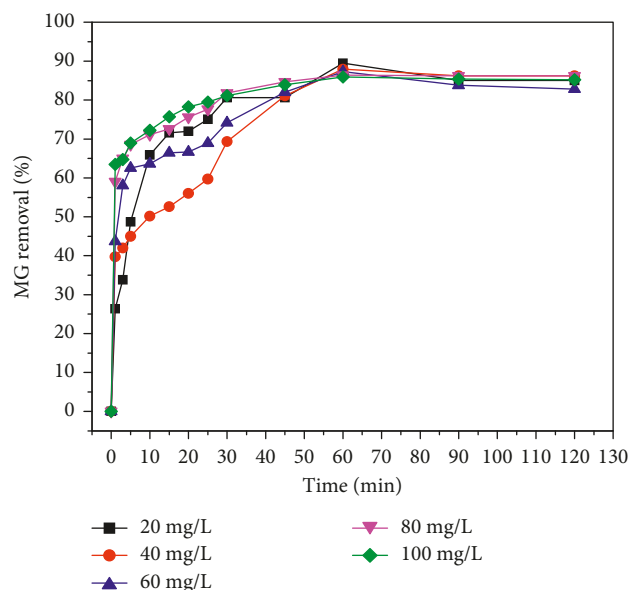


FIGURE 5: Effect of contact time on MG adsorption on TU-poly(AN-co-AA) (adsorbent dosage: 0.5 g; temperature: 298 K; agitation speed: 100 rpm).

attainment. Based on reduction in the number of available active sites, the MG removal percentage gradually slows down. Hence, all the subsequent batch experiments were performed for time of 60 min. Same trend was also observed and reported in [8, 45] for the adsorption of brilliant green and direct yellow 50 (DY50) dyes, respectively.

3.5. Effect of Initial Solution pH. The initial pH of dye solution is a key parameter influencing the adsorption of MG onto TU-poly(AN-co-AA). The range of pH studies choose for MG is 3.0 to 11.0. The reasons of using wide ranges of pH are due to MG sensitivity to pH and to avoid the pH range that may lead to fading and loss of colour intensity. Figure 6 shows the effect of pH on sorption of MG onto TU-poly(AN-co-AA). The maximum and minimum MG removal was observed at pH 5 and pH 11, respectively. MG as cationic dye gives positive charge when dissolved in water. In the acidic medium, the negatively charged surface of the adsorbent tends to attract adsorption of the cationic adsorbate. There is no significant drop or increase in MG adsorption when pH of dye solution was increased. Implying that the adsorption of MG is not solely by electrostatic interaction but other attractive forces like hydrophobic-hydrophobic interaction and hydrogen bonding may dominate significantly. This observation and behaviour was also noticed in [44, 46, 47]. The results submitted that the adsorption of MG onto TU-poly(AN-co-AA) was not strongly influenced by pH since it can be seen that there were only slight variations in the dye uptake from acidic to alkaline conditions. Azha et al. reported similar observation [48]. However, the highest adsorption was observed at pH 5, closed to the ambient pH (4.5); hence, no pH adjustment was made in the following MG experiments.

3.6. Effect of Temperature. The effect of temperature on MG adsorption was studied from 298 to 328 K with other

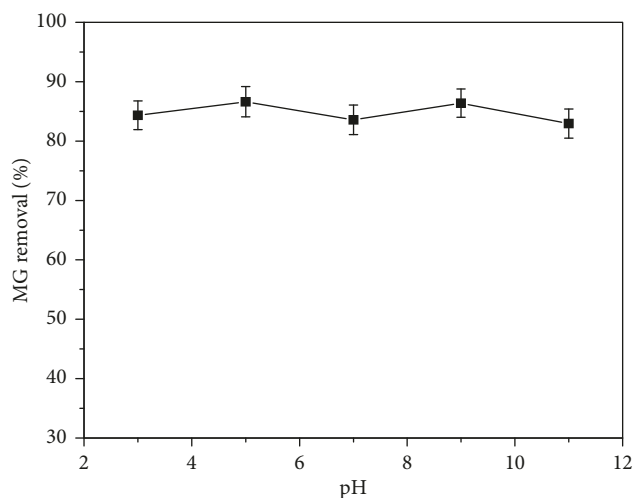


FIGURE 6: Effect of initial pH on MG adsorption onto TU-poly(AN-co-AA) (initial concentration: 50 mg/L; adsorbent dosage: 0.5 g; temperature: 298 K; agitation speed: 100 rpm).

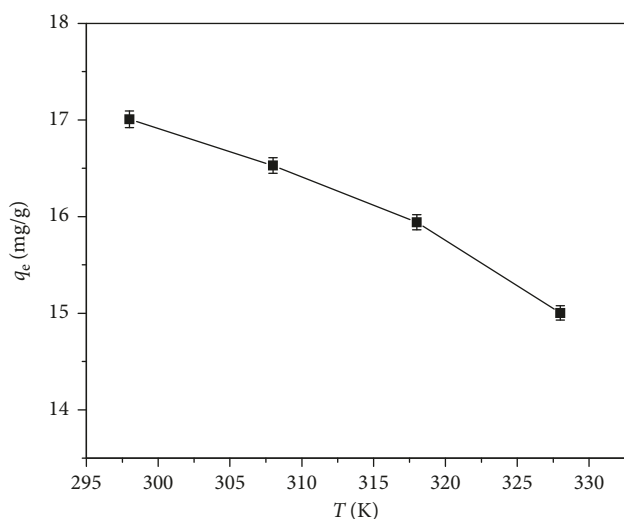


FIGURE 7: Effect of initial temperature on MG adsorption onto TU-poly(AN-co-AA) (initial concentration: 100 mg/L; adsorbent dosage: 0.5 g; agitation speed: 100 rpm).

parameters being kept constant (Figure 7). From the results, it was observed that quantity of MG adsorbed decreases as the temperature was raised. This may be attributed to the fact that, as the temperature was increased, the solubility of MG in solution also increased resulting in stronger interaction forces between MG and solute more than those between MG and TU-poly(AN-co-AA) polymer [49–51]. High temperature might lead to the breaking of existing intermolecular hydrogen bonds between adsorbent and adsorbate, which was found to be an important contribution to the adsorption process. The adsorption capacity q_e for MG removal decreases with an increase in temperature indicating that the adsorption of MG is not favourable at higher temperatures (an exothermic process). This may be associated with the tendency of MG dye ions to escape from the

adsorbent phase to the bulk phase with an elevated temperature of the solution. The decrease in the removal of MG dye with increase in temperature may also be due to weakness of the adsorptive forces between the MG dye molecules and the surface active sites of TU-poly(AN-co-AA) polymer [52].

3.7. Adsorption Kinetic Study. Study of adsorption kinetics is important because the rate of adsorption, which is one of the criteria for efficiency of adsorbent, and the mechanism of adsorption can be established from the kinetic studies. For this study, experimental data were tested using pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models, respectively, and represented in [53–56]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \ln(t),$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (3)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t),$$

$$q_t = k_{IP} t^{0.5} + C_{IP},$$

where q_e (mg/g) and q_t (mg/g) are adsorption capacity at equilibrium and at time t , respectively; k_1 (min^{-1}), k_2 ($\text{g}/\text{mg}\cdot\text{min}$), and k_{IP} ($\text{mg}/\text{g}\cdot\text{min}^{0.5}$) are the rate constants of pseudo-first-order, pseudo-second-order, and intraparticle diffusion; intercept C_{IP} reflects the boundary layer thickness effect; and β (g/mg) and α ($\text{mg}/\text{g}\cdot\text{min}$) are the Elovich constants corresponding to the extent of surface coverage and rate of sorption at zero coverage (initial sorption rate constant), respectively.

Pseudo-first-order and pseudo-second-order kinetic models are limited in identification of roles of diffusion (film or external diffusion; pore diffusion or both) in the adsorption process. In order to fully comprehend the adsorption mechanism, experimental data were also modeled with Elovich and intraparticle diffusion equations [57, 58].

Figure 8 shows the model graphs describing the kinetic characteristic of the adsorption of MG onto the TU-poly(AN-co-AA). Relevant kinetic parameters and correlation coefficients are presented in Table 2. The $q_{e(\text{cal})}$ values were calculated for pseudo-first-order and pseudo-second-order and compared with experimental values as stated in Table 2. The calculated value of $q_{e(\text{exp})}$ for pseudo-first-order kinetic was far from the experimental value, while it showed good agreement in the case of pseudo-second-order, indicating the suitability of the pseudo-second-order kinetic model. The positive value of C_{IP} (12.95 mg/g) of the intraparticle diffusion model indicates surface and faster initial sorption process [59], although the value did not agree with $q_{e(\text{exp})}$. The linear line did not pass through the origin, and this suggests that intraparticle diffusion was not the only limiting mechanism in MG adsorption [58, 60].

The correlation coefficients (R^2) indicated the following order to the fitted kinetic models: PSO > Elovich >

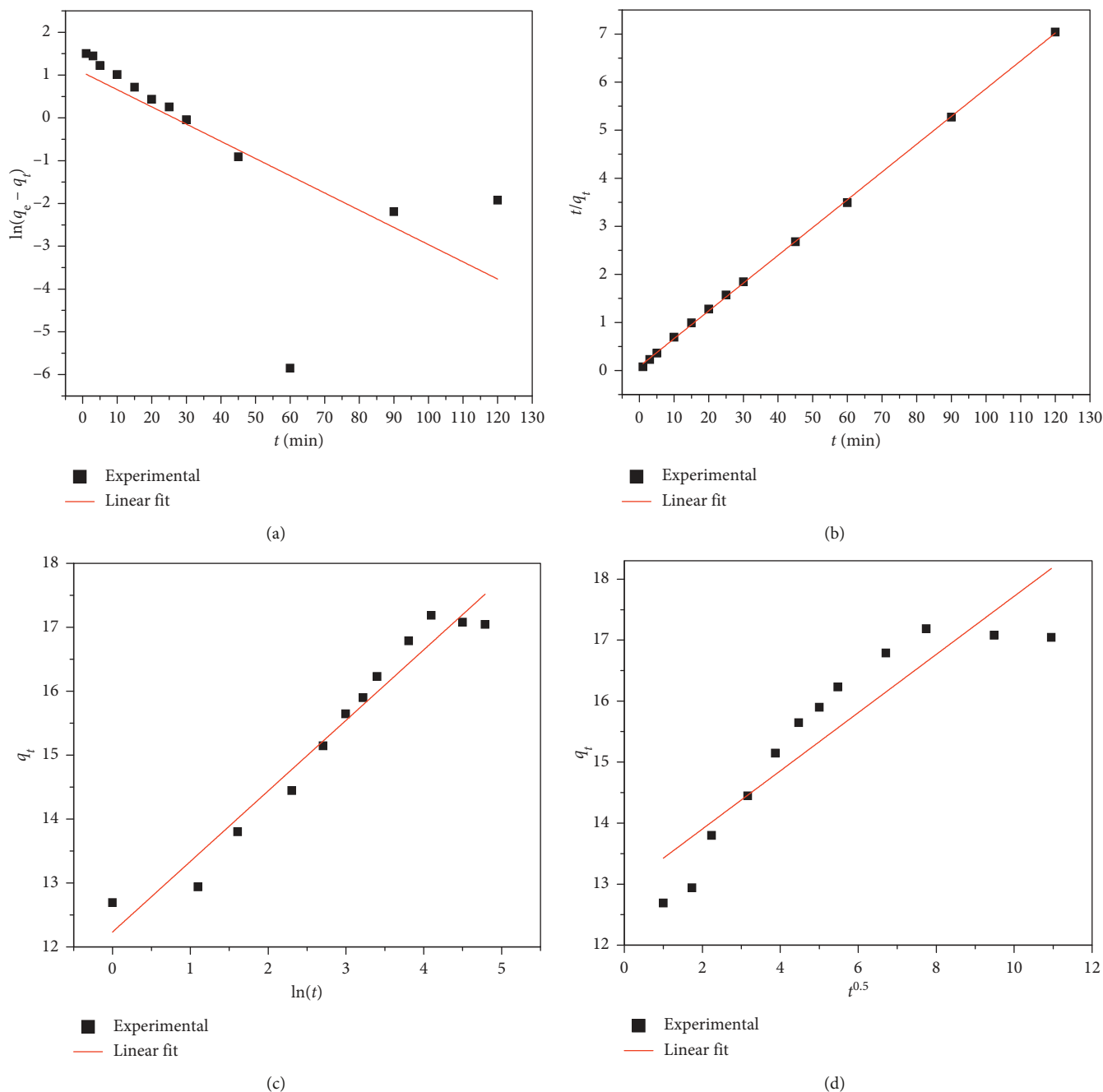


FIGURE 8: Plot of pseudo-first-order (a), pseudo-second-order (b), Elovich kinetic (c), and intraparticle diffusion (d) models.

IPD > PFO. These values suggested that the pseudo-second-order model best described the adsorption process. Therefore, chemisorption was found to be the rate determining step, controlling adsorption of MG onto the TU-poly(AN-co-AA) polymer [61–65]. The sorption process probably involves sharing and or transferring of the electron between adsorbents and adsorbate.

3.8. Adsorption Isotherms. Information regarding the relationship between MG concentration and amount of MG adsorbed on the adsorbent surface when both phases are in equilibrium is given via adsorption isotherms. Three

adsorption isotherm models were tried to obtain the best fit to MG adsorption by TU-poly(AN-co-AA). The isotherm data were fitted to Langmuir, Freundlich, and Temkin models. The linear form of the three models is expressed, respectively, in [53, 66, 67]:

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

$$\ln(q_e) = \ln(K_F) + \left(\frac{1}{n}\right)\ln(C_e), \quad (5)$$

$$q_e = B_T \ln K_T + B_T \ln C_e, \quad (6)$$

TABLE 2: Kinetic parameters and correlation coefficients of MG onto TU-poly(AN-co-AA).

Kinetic models	Parameters			
Pseudo-first-order	k_1 (min ⁻¹) 0.040	$q_{e(\text{exp})}$ (mg/g) 17.19	$q_{e(\text{cal})}$ (mg/g) 2.8866	R^2 0.4533
Pseudo-second-order	k_2 (g/mg·min) 0.0033	$q_{e(\text{exp})}$ (mg/g) 17.19	$q_{e(\text{cal})}$ (mg/g) 17.30	R^2 0.9997
Elovich	β (g/mg) 0.9066	α (mg/g·min) 72113.42		R^2 0.9515
Intraparticle	k_{IP} (mg/g·min ^{0.5}) 0.4769	C_{IP} (mg/g) 12.95		R^2 0.8218

$$R_L = \frac{1}{1 + K_L C_0}, \quad (7)$$

where q_e (mg/g), q_{max} (mg/g), C_e (mg/L), and K_L (L/mg) are defined as the adsorption capacity at equilibrium, the maximum adsorption capacity, the concentration of MG in solution at equilibrium, and the Langmuir constant corresponding to monolayer coverage, respectively.

R_L (equation (7)) is the Langmuir isotherm dimensionless constant (or equilibrium parameter), essentially to define the nature of the adsorption process. $R_L = 0$, $0 < R_L < 1$, $R_L = 1$, or $R_L > 1$ are, respectively, defined as irreversible, favourable, linear, or unfavourable [4, 68, 69].

K_F (mgⁿ/gⁿ) and $1/n$ are Freundlich constant and adsorption intensity or Freundlich exponent.

$1/n = 1$, $0 < 1/n < 1$, and $1/n > 1$ indicate irreversible, favourable, and unfavourable isotherm type, respectively [4].

$B_T = RT/b$ represents the heat of adsorption associated with Temkin's constant, K_T is the equilibrium binding constant corresponding to the maximum binding energy for the Temkin isotherm (L/mg), R represents the universal gas constant (8.314 J/mol·K), and b is a Temkin isotherm constant (J/mol), while T refers to the absolute temperature of the solution (K).

The isotherm data and correlation coefficient obtained from the three different adsorption isotherm models are given in Table 3. Langmuir adsorption isotherm revealed that the data could be fitted into the Langmuir equation well with the correlation coefficient of 0.9309. The value of the separation factor or the equilibrium parameter, R_L , equals 0.6083–0.2369, indicating favourable adsorption of MG onto the TU-poly(AN-co-AA) polymer with 269.54 mg/g of maximum adsorption capacity. Temkin's isotherm data of B_T and K_T established the heat of adsorption and corresponding maximum binding energy of interaction between adsorbate and adsorbent. The correlation coefficient values R^2 for the three models are very close to unity. Based on R^2 values of the adsorption isotherm, Freundlich model is the most appropriate for describing adsorption behaviour of MG onto the modified polymer. In addition, the value of $1/n$ being less unity was observed to be an indication that the adsorption of MG by TU-poly(AN-co-AA) was favourable and not a physical type. It signifies that adsorption occurred on heterogeneous surfaces according to Ayawei et al. and Dabhade et al. [53, 70].

TABLE 3: Isotherm parameters and correlation coefficients of MG onto TU-poly(AN-co-AA).

Isotherm models	Parameters		
Langmuir	K_L (mg/g) 0.0322	q_m (mg/g) 269.54	R^2 0.9309
Freundlich	K_F (L/mg) 1.9004	$1/n$ 0.8359	R^2 0.9960
Temkin	K_T (L/g) 0.6878	b (J/mol) 356.20	R^2 0.9475

3.9. *Thermodynamic Analyses.* Investigating process of adsorption with respect to temperature can give information about thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy change. The effect of temperature on the MG adsorption capacity of TU-poly(AN-co-AA) was performed at 298, 308, 318, and 328 K (Figure 7).

The difference in the extent of the MG adsorption onto TU-poly(AN-co-AA) has been explained on the fundamental of the thermodynamic parameters. The Gibb's free energy change is calculated employing the following equation:

$$\begin{aligned} \Delta G^0 &= \Delta H^0 - T\Delta S^0, \\ \Delta G^0 &= -RT \ln K_d, \end{aligned} \quad (8)$$

where R is the universal gas constant (8.314 J/mol·K), T is the temperature (K), and K_d is the thermodynamic equilibrium constant defined as follows:

$$K_d = \frac{q_e}{C_e}. \quad (9)$$

Stated in equation (10) is the relationship between thermodynamic equilibrium constant, enthalpy, and entropy change defined by the Van't Hoff equation:

$$\ln K_d = \frac{\Delta S^0}{R} = \frac{\Delta H^0}{RT}. \quad (10)$$

The values of ΔH^0 and ΔS^0 were deduced from gradient and intercept of $\ln K_d$ versus $1/T$ plot (Figure 9), and Table 4 shows the values of thermodynamic parameters. The negative values of ΔH^0 (−17.06 kJ/mol) affirms quantitatively that the process is exothermic and MG adsorption process was not favoured at higher temperatures [52, 71]. Therefore, the sorption of MG by TU-poly(AN-co-AA) is feasible, and there

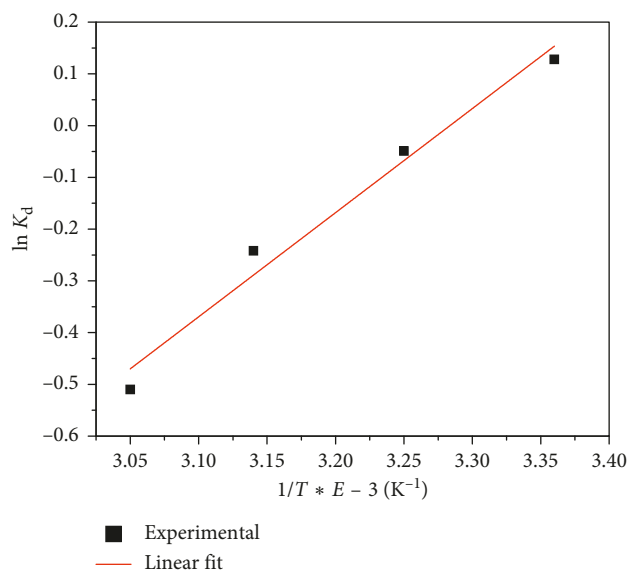


FIGURE 9: Van't Hoff plot for MG adsorption onto TU-poly(AN-co-AA) (MG concentration: 100 mg/L; dosage: 0.5 g; contact time: 60 min; agitation speed: 100 rpm).

TABLE 4: Thermodynamic parameters for adsorption of MG onto TU-poly(AN-co-AA).

Temperature T (K)	Parameters		
	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol.K)
298	-0.38	-17.06	-55.99
308	0.18		
318	0.74		
328	1.30		

is no need for external energy [72]. The spontaneous character of the adsorption process was confirmed by negative values of ΔG^0 , while its positive change suggests that desorption took place at an elevated temperature. In addition, the negative ΔS^0 (change in entropy) value signifies decrease in disorder at adsorbent/solution interface during the sorption process according to Sadaf et al. and Ma et al. [8, 73].

Based on the results of kinetic, isotherm, and thermodynamic analyses, adsorption of MG is exothermic and spontaneous of chemisorption and physisorption process ascribed to the electrostatic interaction between TU-poly(AN-co-AA) and MG. Proposed adsorption mechanism and process kinetic are shown schematically in Figure 10. Adsorption, as a multistage process, involves transfer/sharing of MG ions from bulk solution to the TU-poly(AN-co-AA) surface and diffusion into hydrophilic polymer beads.

3.10. Adsorbent Regeneration and Reusability Study. The reusability of the adsorbents is a key evaluation index in determining the potential of their applications in industry from economic and technological points [69, 74]. Therefore, recoverability and reusability of TU-poly(AN-co-AA) were investigated in the adsorption of cationic MG dye. Five cycle runs on adsorption-desorption were conducted for MG on

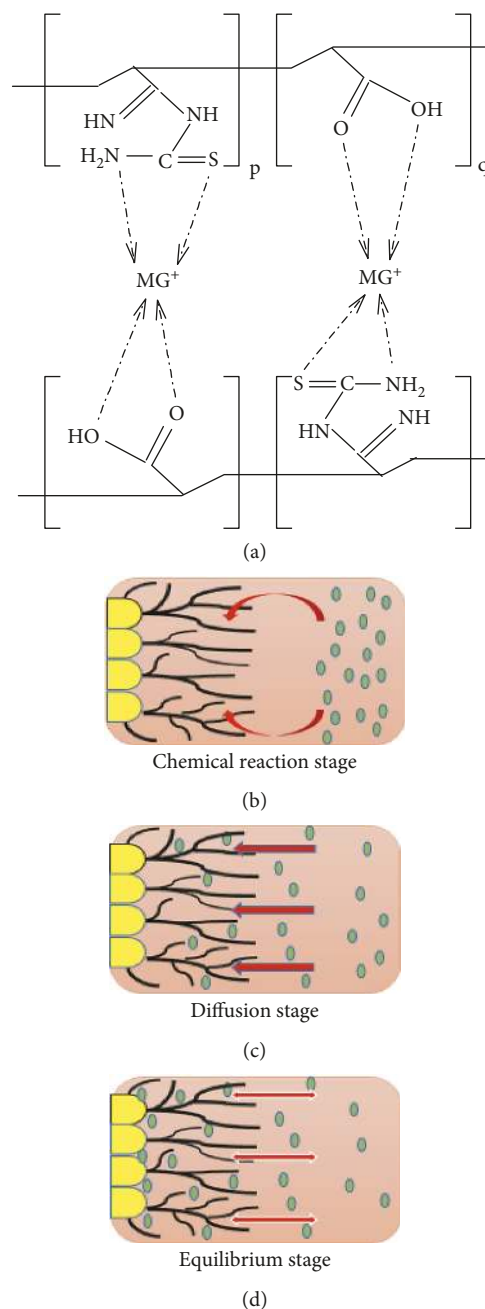


FIGURE 10: Proposed adsorption mechanism (a) and kinetic process (b-d).

TU-poly(AN-co-AA) using mixed solution of 1.0 M HNO_3 and 0.5 M thiourea ($\text{CH}_4\text{N}_2\text{S}$) as desorption solvent (immersed and shaken for 3 h). The adsorbents were washed with distilled water and dried at 50°C in vacuum oven overnight for the next adsorption process. The results indicated that TU-poly(AN-co-AA) could be regenerated and reused with no significant activity depletion. Approximately 89% (Figure 11) efficiency was observed after five consecutive cycles. This established that the prepared TU-poly(AN-co-AA) demonstrated excellent durability and maintained maximum MG sorption capacities for multiple usage.

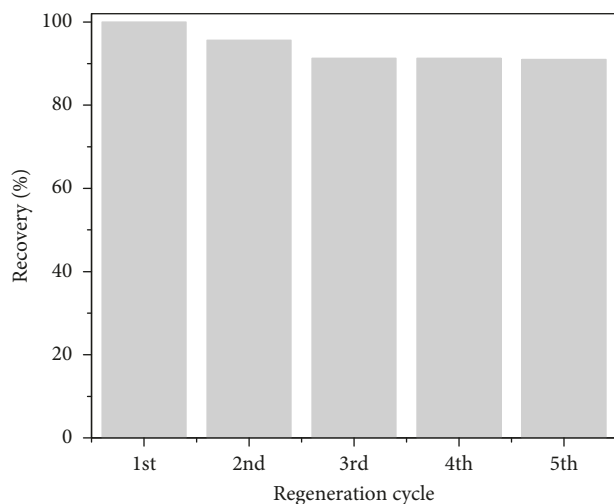


FIGURE 11: Recyclability of TU-poly(AN-co-AA) for adsorption of MG.

4. Conclusions

Poly(acrylonitrile-co-acrylic acid) microspheres were synthesized via the free radical polymerization method and surface modified with thiourea. Prepared TU-poly(AN-co-AA) was used as an adsorbent for the adsorptive removal of malachite green (MG) from aqueous solution in a batch mode. Kinetic studies showed the best fitness of pseudo-second-order model on experimental data. Equilibrium isotherm data were fitted using Langmuir, Freundlich, and Temkin models, and the data were best described by the Freundlich isotherm model. The values of thermodynamic parameters such as change in Gibbs free energy, enthalpy, and entropy revealed the exothermic and spontaneous nature of the adsorption process. TU-poly(AN-co-AA) exhibits high adsorption capacity for malachite green, which is mainly due to the strong electrostatic interactions between negatively charged functional groups of the adsorbent and cationic MG. TU-poly(AN-co-AA) might be an attractive functional material for the adsorptive removal of cationic dyes from wastewater considering its high adsorption capacity (270 mg/g), rapid separation from water, and capacities for multiple usage.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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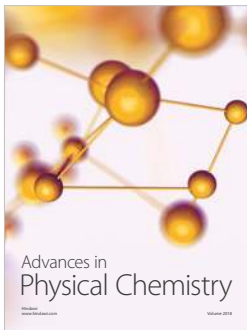
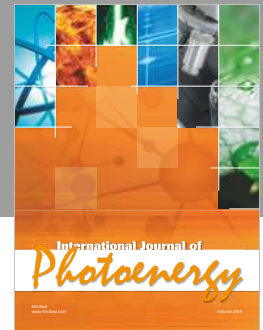
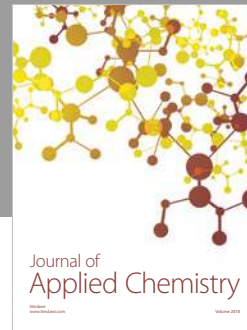
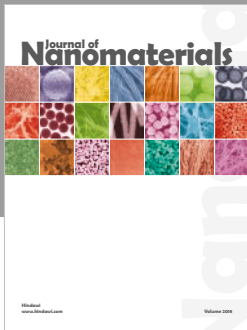
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