

Amidoximated poly(acrylonitrile) particles for environmental applications: Removal of heavy metal ions, dyes, and herbicides from water with different sources

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ABSTRACT: Monodispersed poly(acrylonitrile) [p(AN)] particles were prepared by surfactant free emulsion polymerization and the hydrophobic nitrile groups were converted to hydrophilic amidoxime groups by treatment with hydroxylamine hydrochloride (NH₂OH.HCl) in water. The p(AN) and amidoximated p(AN) [amid-p(AN)] particles were characterized by Fourier transformation infrared (FT-IR) spectroscopy, thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM). The prepared particles were used as adsorbents in the removal from aqueous media of three different types of pollutants; organic dyes methylene blue (MB), and rhodamine 6 G (R6G), a heavy metal ion Cd (II), and a herbicide paraquat (PQ). The effects of various parameters such as amidoximation, pH of solution, amount of particles, and the initial concentration of solution were investigated. Upon amidoximation, a great increase in the adsorption capacity of the prepared particles was observed as the adsorbed amounts were increased to 87, 91, 74, and 91 mg/g from 5, 1.54, 1.06, and 1.22 mg/g for Cd (II), MB, R6G, and PQ, respectively. The amid-p(AN) particles were also able to remove considerable amounts of these pollutants from tap, river, and sea water. Langmuir, Freundlich, and Temkin adsorption isotherms were applied and it was found that the adsorption of Cd (II) and PQ followed the Langmuir adsorption model, whereas the adsorption of MB was found to obey the Freundlich adsorption isotherm. Pseudo first-order and pseudo second-order kinetics were also applied and the results showed that the adsorption processes of Cd (II), PQ, MB, and R6G follow pseudo second-order kinetics. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43032.

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INTRODUCTION

The fast growth of technology and industries developing to fulfill the demands of this modern era are causing environmental pollution, especially air and water pollution. Due to release of industrial effluents into waste water, waters are exposed to harmful pollutants from different sources and become contaminated. Water pollution is and has become a worldwide problem as the earth and water are connected through various cycles involving streams (surface and underground), rains, and sea. As water is the most essential element to sustain living organisms, the contamination of different sources of water by harmful pollutants generates a serious threat for all living organisms. Among the various types of pollutants, heavy metal ions are the

most important as they are very hard to eliminate unless converted to different forms of metal. The heavy metals, including As, Co, Cu, Cd, Pb, Cr, Ni, Hg, and Zn, from many industries, such as mining,¹ tanneries,² metal smelting,³ and batteries,⁴ and so on contaminate water. The presence of these toxic heavy metal ions above tolerance levels can cause accumulative poisoning, cancer, and brain damage in animals.⁵ For example, Cd (II) may cause renal dysfunction, kidney damage, high blood pressure, and even destruction of red blood cells.⁶ Contamination in water is further worsened by the addition of industrial dyes, such as methylene blue (MB) and rhodamine 6G (R6G), and so on. These dyes are released from textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing

industries.⁷ These dyes are added to water from industrial waste and are another source of water pollution. Since dyes are recalcitrant organic molecules, resistant to light, heat, and oxidizing agents as well as to aerobic digestion,^{8,9} wastewater containing dyes is very difficult to treat. A large amount of water is also contaminated by herbicides from agriculture. Paraquat is a non-selective herbicide and is widely used globally due to its quick action in killing unwanted plants. Along with the advantage of quick action of paraquat, it also has destructive effects on human health because it causes pulmonary fibrosis and liver, heart and kidney failure after ingestion as reported by the Center for Disease Control. Due to the potential threats of such water contamination eventually affecting living organisms, removal from water has gained worldwide attention.^{10–12} Different methods, such as reverse osmosis, electrochemical treatments,¹³ precipitation, ion exchange, adsorption,^{14,15} membrane separation, evaporation, coagulation, flotation, hyper filtration,^{15,16} biosorption, and oxidation processes^{17,18} have been developed for the removal of unwanted contamination from waste waters. Since heavy metal cannot be degraded biologically^{19,20} and the degradation products of some dyes are also considered carcinogenic,²¹ their removal from water by adsorption can be considered a more suitable method. In this case, there is no need for degradation of these pollutants, and also after adsorption both the adsorbents and contaminants can be readily removed from water. To date, many types of adsorbents such as activated carbon,²² hydrogels,^{23,24} and polymer particles^{25,26} have been developed and used for the removal of pollutants from water.

Polymer particles based on acrylonitrile can be easily prepared and offer reactive nitrile groups that can be converted into amidoxime groups which have high complex forming ability with heavy metal ions.^{26–28} As monomers with pendent amidoxime groups are not easily available, the most convenient way to obtain amidoxime functional groups is by the conversion of already existing nitriles in monomers such as acrylonitrile and/or nitrile contained in cyanoacrylates. Due to the ease of synthesis of polyacrylonitrile (p(AN)), modification via the conversion of nitriles to amidoxime and ability to form complexes with heavy metal ions, poly(acrylonitrile)-based polymeric structures have been extensively used in the removal of heavy metal ions with different formulations and morphologies.^{24,26,29,30} Maria *et al.* have prepared p(AN-co-DVB) beads and modified the nitrile groups to amidoxime, amidrazone, and oxazoline groups by treating with hydroxylamine, hydrazine, and ethanolamine, respectively.³¹ The modified beads were found as efficient adsorbents for the removal of various heavy metal ions from aqueous medium. The synthesis of nano sized p(AN-co-DVB) particles and modification of nitrile groups to amidoxime groups have also been reported by Eldin *et al.*³² The adsorption characteristics of the p(AN-co-DVB) particles before and after modification were studied for the removal of MB from aqueous medium and an increase in the adsorption capacity was observed after modification of nitriles to amidoximes. Eldin and his coworkers have also prepared nano sized p(AN) particles and treated with hydroxylamine hydrochloride to obtain amidoxime func-

tionized particles.³³ The adsorption capacity of functionalized and unfunctionalized p(AN) particles was investigated for the removal of MB from water and a significant increase in the adsorption capacity was observed after functionalization. Until now, in most studies amidoximes have been used for the removal of heavy metal ions from water, as amidoxime groups form complexes with positively-charged metal ions. This complexing ability of amidoximes with positively charged species can also be utilized to remove other positively charged organic pollutants such as dyes and herbicides from water. Therefore, in this context, monodispersed p(AN) particles were prepared with pendent nitrile groups which were then converted into amidoxime groups for their use in the uptake of cationic organic dyes (i.e., MB and R6G) and a herbicide (PQ) along with a heavy metal ion Cd (II) from aqueous media. Various parameters affecting removal of these pollutants, including the waste water environments, were investigated.

EXPERIMENTAL

Chemicals

Acrylonitrile (AN, $\geq 99\%$, Sigma) as monomer, *N*, *N'*-methylenebisacrylamide (MBA 99%, Acros) as the crosslinking agent, and potassium persulfate (KPS, 99%, Aldrich) as initiator were used. Hydroxylamine hydrochloride (NH₂OH·HCl, 98% Sigma-Aldrich) and sodium hydroxide (NaOH, 98–100.5% Sigma-Aldrich) were used in the amidoximation reaction. Methylene blue (MB, 97%, Fluka) and rhodamine 6G (R6G, Sigma) were used as organic dyes. Cadmium (II) chloride hemipentahydrate (CdCl₂·2.5H₂O 98%, Fluka) was used as a metal ion source, and paraquat was used as herbicide. Sodium hydroxide (NaOH, reagent grade, $\geq 98\%$, Sigma-Aldrich) and hydrochloric acid (HCl, 36.5–38%, Sigma-Aldrich) were used to adjust pH of metal ion solutions. Tap water was collected from the water supply lane in Canakkale Onsekiz Mart University. Sea water was collected from Dardanelles (at Canakkale Strait of Turkey). River water was collected from Karamenderes River at Canakkale, Turkey. Distilled water (DI) was used throughout the experiments.

Synthesis of p(AN) Particles

In a typical synthesis procedure, 4 mL of AN as monomer and 0.094 g of MBA (1 mol % of AN) as crosslinker were added to 90 mL water in a round-bottom flask and stirred at 800 rpm to prepare a homogenous mixture. Temperature of the reaction medium was increased to 80°C in an oil bath and the reaction mixture was continuously stirred at 800 rpm. After 15 min, 0.1648 g of KPS (1 mol % of AN) was first dissolved in 5 mL DI and then added to the reaction mixture to initiate the polymerization and crosslinking reaction. After 10 min, the addition of the KPS solution, the color of the reaction mixture turned milky giving an indication that polymerization had begun. The polymerization reaction was allowed to proceed for a further 5 h. At the end of the reaction time, heating and stirring was stopped and the temperature of the reaction mixture was allowed to decrease to room temperature. In order to remove unreacted monomer and crosslinker, the prepared p(AN) particles were centrifuged at 10,000 rpm, and washed with DI five

times. Finally, p(AN) particles were dried at 60°C in an oven and used for characterization and as adsorbents. The SEM image of the prepared p(AN) particles was recorded by scanning electron microscope (SEM, JEOL 2010).

Amidoximation Reaction

Amidoximation of the pendant nitrile groups was carried out by treating the p(AN) particles with hydroxylamine hydrochloride. Briefly, 1.5 g (3 times excess compared to number of moles of nitrile groups in p(AN) particles) of $\text{NH}_2\text{OH}\cdot\text{HCl}$ was dissolved in 100 mL DI and was neutralized by the addition of NaOH. Then, 1 g of dried p(AN) particles were added to the $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution. The reaction was allowed to proceed for 24 h at 80°C in an oil bath. At the end of the reaction time, temperature of the reaction medium was decreased to room temperature. Amidoximated p(AN) (amid-p(AN)) particles were washed with DI by centrifugation at 10000 rpm for 10 min followed by the removal of the supernatant solution and redispersing in DI and re-centrifugation five times. Finally, the clean amid-p(AN) particles were dried in an oven at 60°C for 24 h and used for characterization and as adsorbents. The conversion of nitrile groups to amidoximes was confirmed by Fourier Transformation Infrared (FT-IR, Thermo Scientific, Nicolet iS 10) Spectrophotometer. Thermal properties of the p(AN) beads before and after amidoximation were investigated by Thermogravimetric Analyzer (SII TG/DTA 6300 model).

Adsorption Experiments

The ability of the prepared p(AN) to adsorb contaminants from water was investigated by using p(AN) particles before and after amidoximation as adsorbents for the removal of a heavy metal ion Cd (II), organic dyes such as MB and R6G and a herbicide PQ from aqueous solutions at room temperature. In a typical procedure, for the adsorption of Cd (II), 100 ppm, 100 mL solutions of Cd (II) were placed in separate beakers, and pH of these solutions was adjusted to 2, 4, 5, 6, and 7. The pH of Cd (II) solutions was adjusted by using 0.5M HCl or 0.5M NaOH aqueous solutions and was measured by a Sartorius Documeter pH meter. After adjustment of pH, 50 mg of dried p(AN) or amid-p(AN) was added to the solution and adsorption was allowed to take place at 400 rpm. After specific intervals of time, 0.2 mL samples were taken from the adsorption medium, diluted 30 times by the addition of DI and the amount of Cd (II) was measured by Atomic Absorption Spectrophotometer (Thermo Scientific, ICE 3000 series, AAS). Effect of initial concentration of solution was studied by carrying out the adsorption reaction with Cd (II) solutions of different initial concentrations; 50, 100, 150, 200, and 250 ppm with 100 mL volume and keeping all other parameters such as amount of adsorbent, pH, etc. constant. The effect of different amounts of adsorbent was also investigated by using 0.025, 0.05, 0.075, 0.10, and 0.125 g of adsorbent to adsorb Cd (II) from 100 mL, 100 ppm Cd (II) solution. Adsorption of PQ was carried out by using 0.05 g of adsorbent to adsorb PQ from 100 mL solution with different initial concentrations; 50, 100, 150, 200, and 250 ppm. The samples with 0.5 or 1 mL volume were withdrawn, diluted by 4–20 times depending upon initial concentration of solution, and amount of PQ was measured by UV–Visible spectrophotometer (UV–Vis, T80+, PG Instruments) at

its maximum absorption wavelength of 257 nm. The adsorbed amount was determined from a calibration curve constructed at 257 nm. For the adsorption of MB and R6G, 0.05 g of adsorbent was used for their removal from separate 100 mL solutions of MB (1.6×10^{-4} M) and R6G (1×10^{-4} M). During the adsorption experiment, the solutions were stirred at 400 rpm and 0.5 mL samples were withdrawn, diluted with DI, and the amount of MB and R6G was measured by UV–Visible spectrophotometer at their maximum absorption wavelengths of 664 and 530 nm for MB and R6G, respectively. Again the adsorbed amounts of dyes were calculated from the calibration curves constructed at these wavelengths: 664 and 530 nm for MB and R6G, respectively. Additionally, the effect of different initial concentration of MB was also investigated by using different initial concentrations of MB (i.e., 0.8×10^{-4} to 2.4×10^{-4} M).

RESULTS AND DISCUSSION

Synthesis and Amidoximation of p(AN) Particles

Schematic representation of the synthesis of p(AN) particles and the amidoximation of nitrile groups is shown schematically in Figure 1(a). In the first step, p(AN) particles of almost homogenous shape and size were prepared by surfactant-free emulsion polymerization at 80°C.

The persulfate ions ($\text{S}_2\text{O}_8^{2-}$) which are produced from the initiator (KPS) decomposed to produce sulfate radicals (SO_4^-) initiating the polymerization and crosslinking of AN. During the reaction small primary particles and surface active oligomers aggregate with each other to form polymer particles, and the aggregation is stopped when electric charge at their surface increases to such an extent that it can prevent further aggregation. The electric charge is created due to the presence of sulfate groups on the polymer chains. In the second step, the hydrophobic nitrile groups were converted to hydrophilic amidoxime groups by treating with NaOH-neutralized $\text{NH}_2\text{OH}\cdot\text{HCl}$. A certain amount of NaOH (equivalent to HCl) was added to neutralize the HCl content of NH_2OH . HCl, and the reaction was continued at 80°C for 24 h. Upon amidoximation, the milky color p(AN) particles turned light yellow as can be seen from digital camera images of p(AN) and amid-p(AN) given in Figure 1(a). This color change from milky white to light yellow as a result of the amidoximation reaction can be attributed to the amidoximation reaction and the more hydrophilic nature of amid-p(AN) particles.^{29,34} A similar color change was also observed by Neghlani *et al.*³⁵ after converting the pendent nitrile groups of p(AN) mats to amidoxime groups. The SEM image of the prepared p(AN) particles is shown in Figure 1(b). It is obvious that p(AN) particles are almost monodispersed with homogeneous spherical shape and diameters of the particles were approximately 400–500 nm.

The polymerization of acrylonitrile and the conversion of nitrile groups to amidoxime groups were confirmed by FT-IR spectroscopy. The FT-IR spectra of p(AN) and amid-p(AN) are given in Figure 2(a).

The absorption peaks at 2247 cm^{-1} and 1078 cm^{-1} are due to $-\text{CN}$ stretching and bending vibrations, respectively. The absorption peak at 2940 cm^{-1} is due to $-\text{C}-\text{H}$ stretching

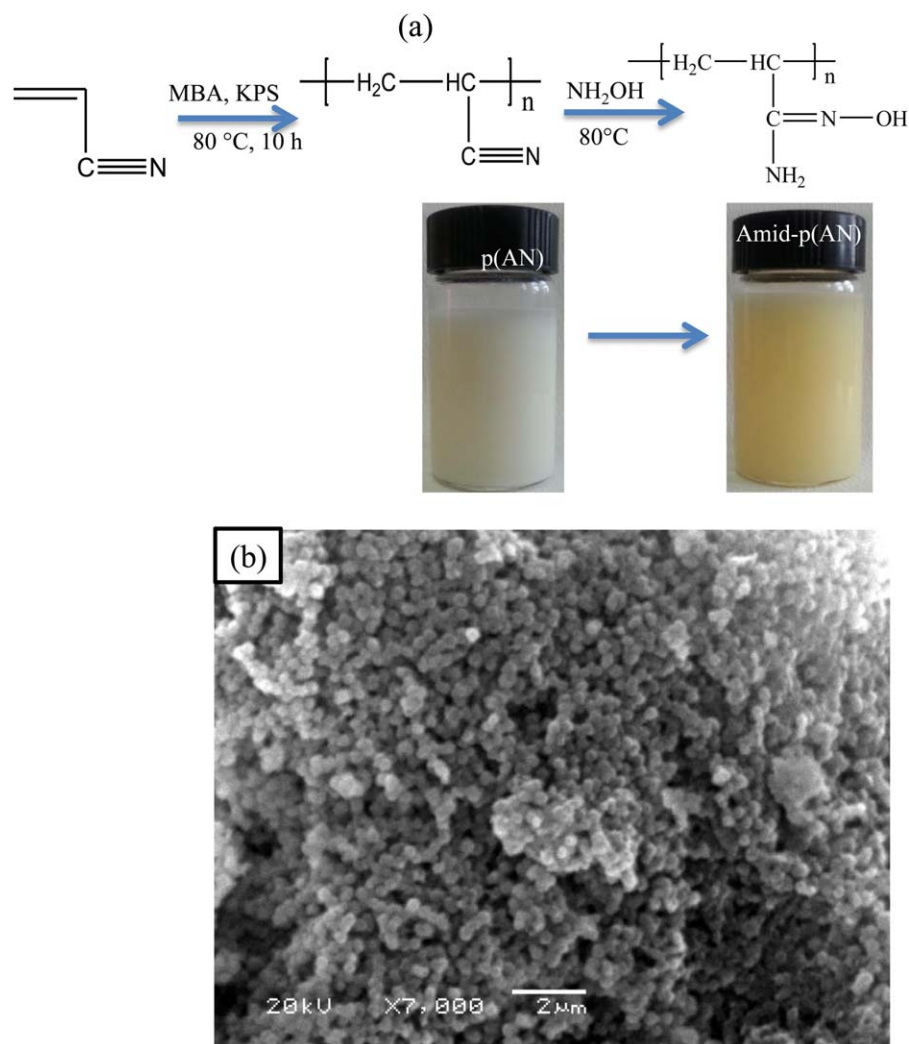


Figure 1. (a) Schematic representation for the synthesis p(AN) and amidoximation reaction, and digital camera images of p(AN) and amid-p(AN) suspended in water (b) SEM image of p(AN) particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vibrations, whereas the peak at 1560 cm^{-1} corresponds to —C—H inplane deformation vibration of —CH_2 groups. As a result of the amidoximation reaction, nitrile groups were converted to amidoxime groups and this conversion is clearly demonstrated by FT-IR spectra of the amid-p(AN) particle as illustrated in Figure 2(a). It can undoubtedly be seen that after the amidoximation reaction, the absorption peak of nitrile groups completely disappeared which indicates that all the nitrile groups were converted to new amidoxime groups. After amidoximation, a broad band around 3300 cm^{-1} appears due to the —OH groups in amidoxime. The absorption bands at 1653 and 920 cm^{-1} correspond to —C=N and —N—O of amidoximes. So, FT-IR spectra confirm that nitrile groups were converted to amidoxime groups.^{36,37} Thermal properties of the p(AN) particles before and after amidoximation were also investigated and their matching thermograms are illustrated in Figure 2(b). For p(AN) particles, the thermal degradation began at 250°C and 34.6% weight loss occurred upon heating up to 570°C . Upon further heating, the degradation rate increased, and a total of 99% weight loss occurred as the temperature

reached 720°C . After amidoximation, the thermal degradation behavior of p(AN) particles completely changed. Thermal degradation of amid-p(AN) began at 100°C , and 5% weight loss was observed upon heating to 210°C , and upon further heating the degradation rate rose and weight loss increased to 50% when the temperature increased to 440°C . Upon heating above 440°C , the degradation rate further speeded up and weight loss increased to 90% at 556°C . The total weight loss increased to 98.5% as the heating temperature was raised to 880°C . Different thermal degradation confirms that a variation in chemical structure occurred in p(AN) particles after the amidoximation reaction which is the conversion of nitriles to amidoximes on p(AN) chains.

Adsorption Study

The adsorption ability of p(AN) and amid-p(AN) particles were investigated for use as adsorbents in the removal of three different types of water contaminants: a heavy metal ion, Cd (II); a herbicide, PQ; and organic dyes, MB and R6G. The maximum amount of dyes, herbicide or Cd (II) adsorbed per gram of dry

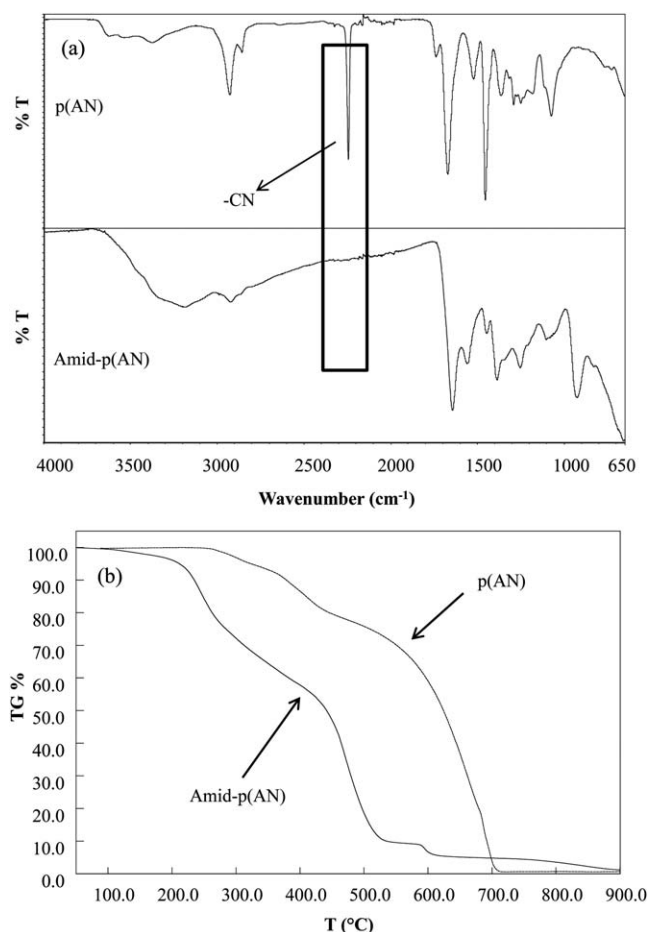


Figure 2. (a) FT-IR spectra of p(AN) before and after amidoximation and (b) TGA thermograms of p(AN) particles before and after amidoximation reactions.

p(AN) or amid-p(AN) was calculated by using the following mass balance equation.

$$q = (C_o - C_e)V/W \quad (1)$$

where q is the adsorbed amount of adsorbent in mg/g, C_o is the initial, and C_e is the equilibrium concentration (ppm) of adsorbate in aqueous solution. V is the volume of adsorbate solution in L and W is the mass of p(AN) or amid-p(AN) particles used as adsorbents. It has been reported that adsorption capacity of amidoximes is very high compared to adsorbents which contain nitrile groups. Therefore, firstly the effect of amidoximation of the pendent nitrile groups on the adsorption capacity of the prepared particles was investigated. For this comparative study, separate 100 mL solutions of Cd (II) (100 ppm), MB (1.8×10^{-4} M), R6G (1×10^{-4} M), and PQ (100 ppm) were prepared and 0.05 g of p(AN) or amid-p(AN) particles were used as adsorbent. As can be seen from Figure 3, a tremendous increase in the adsorption capacity was observed for amid-p(AN) particles. This large increase in the adsorption capacity can be attributed to greater complexation tendency of amidoxime groups with oppositely or positively charged water contaminants or better binding ability than nitrile groups for the mentioned adsorbates.

As the solubility of Cd (II) in water is pH dependent, at low solution pH values Cd (II) remains soluble in water but at high pH its solubility is decreased due to the formation of $\text{Cd}(\text{OH})_2$ which is precipitated. So, in order to determine the optimum pH at which the maximum amount of Cd (II) can be adsorbed, the effect of pH of solution on the adsorption of Cd (II) was studied. For this purpose, 100 mL, 250 ppm solutions of Cd (II) were prepared, and pH was adjusted from 2 to 7 by using 0.5M NaOH or 0.5M HCl aqueous solutions. The adsorption of Cd (II) by amid-p(AN) as a function of pH is shown in Figure 4(a) and as can be seen the amount of Cd (II) adsorbed on amid-p(AN) increased as the pH of the Cd (II) solution increased from 2 to 6. However, with further increase in pH of the Cd (II) solution, the adsorbed amount of Cd (II) decreased. This decrease in the amount of adsorbed Cd (II) can be attributed to the precipitation of Cd (II) in the form of $\text{Cd}(\text{OH})_2$ which is produced and precipitated in the presence of excess OH^- in the reaction medium. As the maximum adsorption was observed at solution pH of 6; therefore, all other adsorption experiments for Cd (II) were conducted at pH 6. In the previous study by Maria *et al.*, the optimum pH for maximum adsorption of Cd (II) from water was reported as 9.³¹ The contradiction in these results may be due to the reason that Maria *et al.* have used standard solution of Cd (II), while in the present study $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ was used as a source of Cd (II) ion, and it was precipitated as the pH was increased from 6 to higher values in the investigated concentration range. Therefore, the optimum pH for the maximum adsorption of Cd (II) depends upon the source of Cd (II) e.g., the different sources or salts of Cd (II) may have different dissociation behavior in water and precipitate at different pH of the medium. In addition, the pH at which Cd (II) is precipitated also depends upon total volume and concentration of solution. As there is a change in concentration or total volume of solution, the number of Cd (II) ions are changed, so the amount of base or the value of pH to precipitate Cd (II) is also changed. Maria *et al.*³¹ have used 10 mL, 80 ppb solution of Cd (II) thereby the total volume is

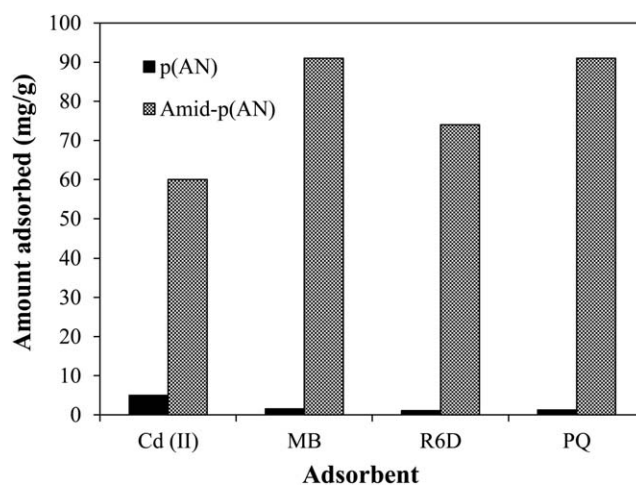


Figure 3. Comparison of adsorption capacity of p(AN) particles before and after amidoximation. Reaction conditions; 100 ml solution of Cd (II) (100 ppm and pH = 6), PQ (100 ppm), MB (1.6×10^{-4} M), and R6G (1×10^{-4} M), 0.05 g of amid-p(AN), 400 rpm, room temperature.

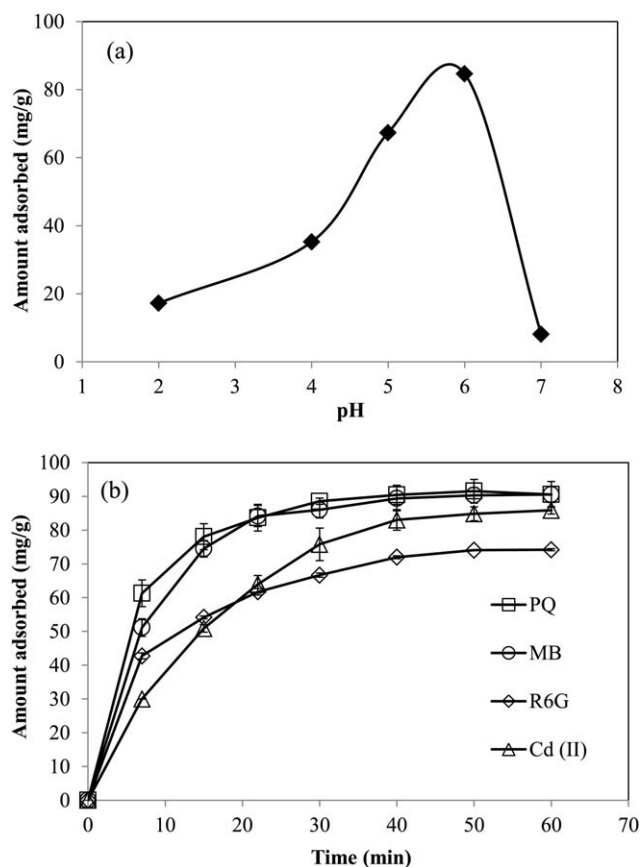


Figure 4. (a) Effect of pH of medium on the removal of Cd (II) by amid-p(AN) particles, (b) the plots of adsorbed amount of PQ, MB, R6G, and Cd (II) as a function of time. Reaction conditions; 100 mL solution of Cd (II) (250 ppm and pH = 6), PQ (100 ppm), MB (1.6×10^{-4} M), and R6G (1×10^{-4} M), 0.05 g of amid-p(AN), 400 rpm, room temperature.

quite different from the present study; therefore, the optimum pH for Cd(II) ion precipitation and the maximum removal amounts from aqueous medium is also different. Moreover, the used adsorbent can also effect the adsorption process as amid-p(AN) particle possesses ionize able groups to bind to the positively charged species. For the adsorption of MB, R6G, and PQ, the prepared aqueous solutions were used for adsorption experiments. The amount of Cd (II), MB, R6G, and PQ adsorbed is given in Figure 4(b), where the adsorption rates of each pollutant was high in the initial stages but they all steadily slowed with the passage of time. Maximum adsorption was achieved in 40 min, and after that no change in the adsorbed amounts of adsorbates was observed with time after about 50 min. The decrease in the adsorption rate with the passage of time can be attributed to the decrease in concentration gradient between solution and the surface or interior of amid-p(AN) particles. Once the maximum adsorption was achieved, then the adsorption rate also became equal to zero and no more adsorbate was adsorbed on the adsorbent. The time required for the removal of maximum amount of MB is very less as compared to the previous reported literature where Eldin *et al.* used amidoximated p(AN-co-DVB) for the removal of MB from water and that the adsorption equilibrium was established after 7 h.³² The

quick adsorption characteristics of the current amid-p(AN) proves that these beads are superior than the previously reported adsorbents. As it can be seen from Figure 4(b), 90 mg of MB was adsorbed by per gram of dried amid-p(AN). This adsorbed amount of MB is also very high as compared to that reported by Eldin *et al.*³³ for the removal of MB by nano sized amidoximated p(AN) particles.

Since the initial concentration of the solution also affects the adsorption rate and the adsorbed amount; this was also studied for the removal of Cd (II). Solutions of Cd (II) with different concentrations (50, 100, 150, 200, and 250 ppm) were prepared and pH was adjusted to 6 at which the maximum amount of Cd (II) was adsorbed. Dried amid-p(AN) particles of 0.05 g were added as adsorbent to 100 mL solutions of Cd (II) with each concentration. The amounts of Cd (II) adsorbed from the solutions with different concentrations are shown in Figure 5(a). An increase in the amount of Cd (II) adsorbed by amid-p(AN) particles was observed with the increase in initial concentration of Cd (II) solution, as can be seen from Figure 5(a). The increase in the adsorbed amount of Cd (II) can be attributed to the increase in the amount of Cd (II) available in the

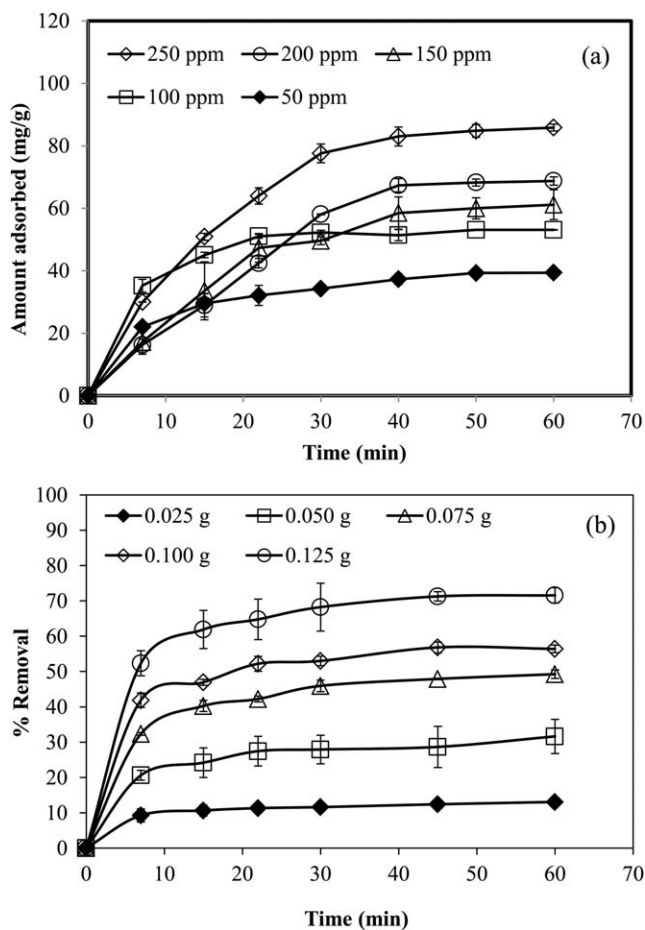


Figure 5. (a) The plots of the amount of adsorbed Cd (II) by amid-p(AN) particles as a function of time form different initial metal ion concentrations [amid-p(AN) particles: 0.05 g]. (b) Plots of % removal of Cd (II) as function of time with different amounts of amid-p(AN) particles [Cd (II): 100 mL, 100 ppm, pH 6].

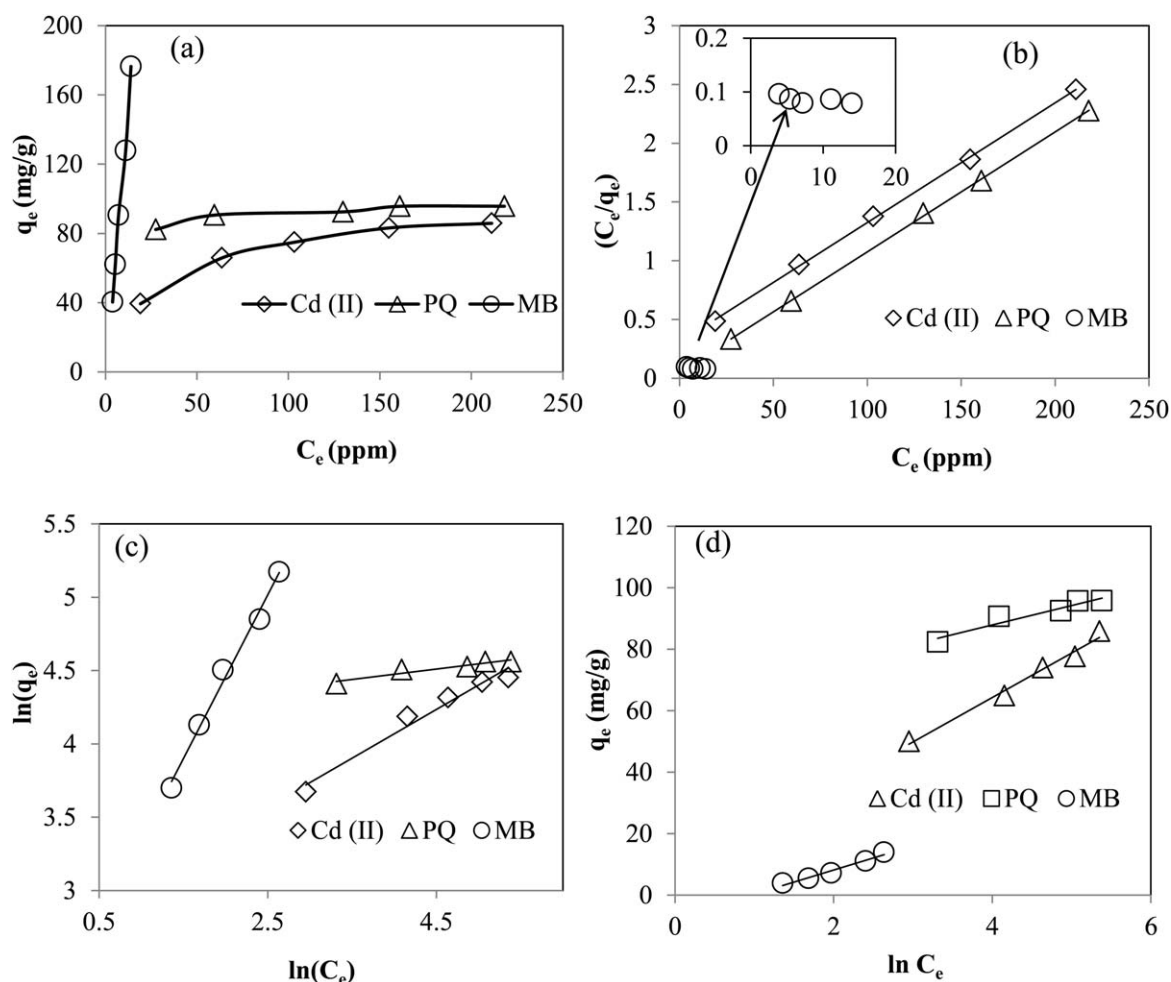


Figure 6. (a) The graph of q_e against C_e and the application of (b) Langmuir (c) Freundlich, and (d) Temkin adsorption isotherms to the adsorption of Cd (II), PQ, and MB by amid-p(AN).

solution for amid-p(AN) particles. The effect of amount of adsorbent was also evaluated by using five different amounts of amid-p(AN) particles (e.g., 0.025, 0.05, 0.075, 0.010, and 0.0125 g) to adsorb Cd (II) from 100 mL, 100 ppm aqueous solution at pH 6. It is obvious that the amount of Cd (II) adsorbed increased with the increase in the amount of adsorbent. By increasing the amount of adsorbent, the number of sites available for adsorption of Cd (II) increased so higher amounts of Cd (II) were adsorbed, as illustrated in Figure 5(b) in terms of % removal. The % removal increased from 13 to 72% by increasing the amount of amid-p(AN) from 0.025 to 0.0125 g. This is also the case in adsorption studies of most metal ions and/or organic compounds.^{24,26,29,30} The % removal of Cd (II) in the present investigation is very high as compared to that reported by Maria *et al.*³¹ where they observed only 46% removal of Cd (II) from 10 mL, 80 ppm solution of Cd (II) by using relatively larger amount of adsorbent, i.e.; 1 g of amidoximated p(AN-co-DVB) beads as adsorbents.

Adsorption Isotherms

In order to determine the nature of adsorption, the effect of initial concentrations of Cd (II), MB, and PQ on the adsorption by amid-p(AN) were also investigated by applying different

adsorption isotherms. For the adsorption of Cd (II), MB and PQ, the plots of q_e versus C_e are given in Figure 6(a). In the construction of the Langmuir adsorption isotherm, it is assumed that the surface of the adsorbent is homogenous, all adsorption sites are equivalent, and a monolayer of adsorbate is formed on the surface of adsorbent. The Langmuir adsorption isotherm was plotted using the well-known Langmuir equation, which is given below:

$$C_e/q_e = C_e/q_m + 1/q_m K_L \quad (2)$$

where C_e is equilibrium concentration of the solution in ppm, q_e is the amount of adsorbate (mg/g) adsorbed per gram of dried amid-p(AN) particles, q_m is the maximum amount of adsorbate (mg/g) adsorbed per gram of dried amid-p(AN) particles, while K_L is the Langmuir adsorption equilibrium constant. Langmuir adsorption isotherms were constructed for Cd (II), MB, and PQ by plotting C_e/q_e as a function of C_e as shown in Figure 6(b). The linear pattern of Langmuir adsorption isotherms with coefficient of determination (R^2) values of 0.9995 and 0.9997 for Cd (II) and PQ, respectively, demonstrate that Cd (II) and PQ are adsorbed on the amid-p(AN) particles in the form of a monolayer. Additionally, the maximum amounts of adsorption of Cd (II) and PQ calculated from Langmuir

adsorption isotherms are 98.04 mg/g which is very close to experimentally observed values of 87 and 96 mg/g for Cd (II) and PQ, respectively. This close resemblance of the experimentally observed values with the values calculated from the Langmuir adsorption isotherm supports the idea that the adsorption of Cd (II) and PQ can be represented by the Langmuir adsorption isotherm. On the other hand, an R^2 value of 0.4428 for MB was obtained when the Langmuir adsorption isotherm is applied, which indicated that the adsorption of MB was not in a monolayer. The nonlinear pattern of Langmuir adsorption isotherm for MB was given in the inset of Figure 6(b). As the effect of surface roughness is not considered by the Langmuir adsorption isotherm, the possibility of different types of adsorption sites is also not considered. In order to take into consideration the effect of surface roughness and availability of different types of adsorption sites, Freundlich adsorption isotherms were also applied to adsorption data of Cd (II), PQ, and MB. The Freundlich adsorption isotherm was plotted using the Freundlich equation, which is given below:

$$\log q_e = \log K_F + 1/n \log C_e \quad (3)$$

where q_e is the amount of adsorbate in mg/g adsorbed at equilibrium state of adsorption, C_e is the equilibrium concentration of adsorbate solution, while K_F and n are the equilibrium constants that represent the adsorption capacity and adsorption intensity, respectively. Freundlich adsorption isotherms for Cd (II), PQ, and MB were constructed by plotting $\log q_e$ versus $\log C_e$ as shown in Figure 6(c). The nonlinear pattern for Cd (II) and PQ, which is also clear from their R^2 values of 0.9695 and 0.9222, indicates that the adsorption of Cd (II) and PQ did not follow the Freundlich adsorption isotherm. However, the R^2 value for the Freundlich adsorption isotherm of MB is very close to 1 (i.e., 0.9908) therefore, the adsorption of MB by amid-p(AN) obeys the Freundlich adsorption isotherm. Both the Langmuir and Freundlich adsorption isotherms ignore the possibility of interaction between adsorbent and adsorbed species where the presence of such types of interaction can exist and may also affect the adsorption process. Therefore, in order to consider this effect, the Temkin adsorption isotherm was also applied, which takes into account the effect of possible interactions between adsorbent and adsorbates that are adsorbed on the adsorbent. The Temkin adsorption isotherm is based on the assumption that free energy of sorption is a function of surface coverage of adsorbent. The mathematical expression of the Temkin adsorption isotherm is given as follows:

$$q = B \ln K_T + B \ln C_e \quad (4)$$

where, q_e is the amount of adsorbate adsorbed (mg/g) on amid-p(AN) at equilibrium state, K_T is known as the equilibrium binding constant and corresponds to maximum binding energy, C_e represents the concentration of adsorbate in solution at equilibrium conditions, and the parameter B is related to binding energy and its value can be calculated by the following mathematical expression:

$$B = RT/b_T \quad (5)$$

where R is the universal gas constant, T represents the temperature in Kelvin, and b_T is the Temkin isotherm constant. Accord-

Table I. Kinetic Parameters for the Adsorption of Cd (II), PQ, and MB by Amid-p(MAc-co-AN) Microgel from the Application of Langmuir, Freundlich, and Temkin isotherms (Metal Ion Concentration 50–250 ppm, 100 mL)

Isotherm	Constants	Adsorbent		
		Cd (II)	PQ	MB
Langmuir	K_L (L/g)	0.033	0.183	0.012
	q_m (mg/g)	98.04	98.04	909.1
	R^2	0.999	0.999	0.443
Freundlich	K_F (L/g)	15.46	66.02	9.27
	n	3.00	14.06	0.896
	R^2	0.969	0.922	0.991
Temkin	B	14.47	6.33	7.88
	K_T (L/g)	1.55	19571.56	0.38
	R^2	0.986	0.928	0.9717

ing to eq. 4, the Temkin adsorption isotherm can be constructed by plotting q_e as a function of $\ln C_e$ and is shown in Figure 6(d). The constants B and K_T were calculated from the slope and intercept, respectively.

Kinetic parameters calculated from Langmuir, Freundlich, and Temkin adsorption isotherms for the adsorption of Cd (II), PQ, and MB are given in Table I. As can be seen from Table I, Cd (II), and MB adsorption from aqueous environments by amid-p(AN) followed the Temkin isotherms better than PQ adsorption. The same result is obtained when the Freundlich isotherm is applied.

Adsorption Kinetics

Adsorption kinetics were investigated in terms of order and rate constants. Pseudo first-order and pseudo second-order kinetic models were applied and corresponding rate constants and orders were calculated.

Pseudo First-Order Kinetics. The experimental data for the adsorption of Cd (II), PQ, MB, and R6G was treated with pseudo first-order kinetics by applying the mathematical expression proposed by Lagergren, which is given as the following:

$$\log (q_e - q_t) = \log q_e - k_1 \cdot t/2.303 \quad (6)$$

where q_e and q_t are the amounts of adsorbate (mg/g) which were adsorbed on the adsorbent at equilibrium time and at time t (min), and k_1 (min^{-1}) is the rate constant of pseudo first-order kinetics. Equation 6 is a straight line equation and the straight line was obtained by plotting $\log (q_e - q_t)$ versus t as shown in Figure 7(a). Values of k_1 and q_e were calculated from slope and intercept, respectively. Values of k_1 , q_e , and R^2 are given in Table II.

Pseudo Second-Order Kinetics. The adsorption data was also treated with a pseudo second-order kinetic model by applying the following equation:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

where q_e and q_t are the amounts of adsorbate (mg/g) which were adsorbed on the adsorbent at equilibrium time and at

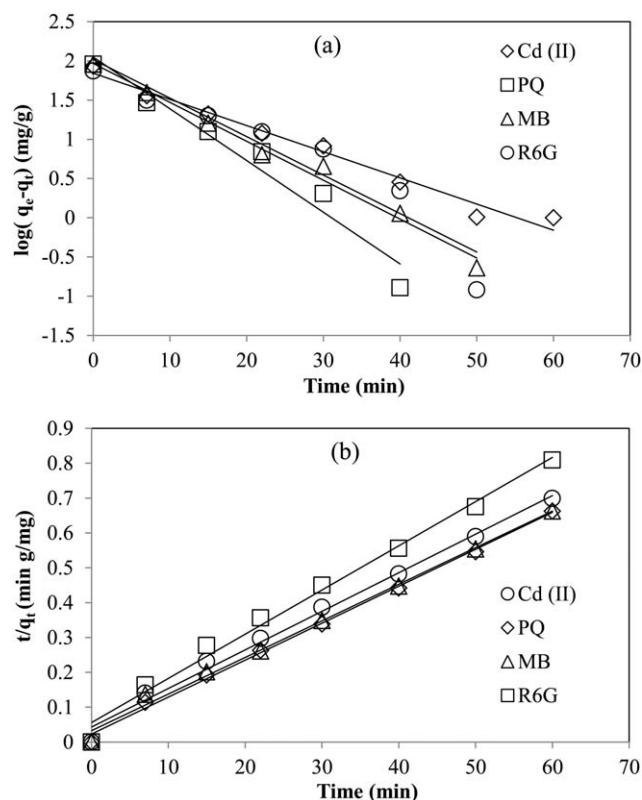


Figure 7. (a) Application of pseudo first order and (b) pseudo second-order kinetics to the adsorption of Cd (II), PQ, MB, and R6G. Reaction conditions: 100 mL solution of Cd (II) (250 ppm and pH = 6), PQ (100 ppm), MB (1.6×10^{-4} M), and R6G (1×10^{-4} M) 0.05 g of amid-p(AN), 400 rpm, room temperature.

time t (min), and k_2 (g/mg min) is the rate constant of pseudo second-order kinetics. The straight line was constructed by plotting t/q_t as a function of t as shown in Figure 7(b).

Table II. Kinetic Constants of Pseudo First-Order and Pseudo Second-Order Kinetics for the Adsorption of Cd (II), PQ, MB, and R6G

Kinetics	Constants	Adsorbent			
		Cd (II)	PQ	MB	R6G
Pseudo-first order	k_1 (min^{-1})	0.077	0.152	0.114	0.113
	q_e (mg/g)	69.53	111.91	92.85	103.56
	R^2	0.978	0.954	0.987	0.901
Pseudo-second order	k_2 (g/mg min)	0.003	0.005	0.003	0.003
	q_e (mg/g)	90.09	94.34	95.23	78.74
	R^2	0.992	0.997	0.994	0.989

[Reaction conditions; 100 mL solution of Cd (II) (250 ppm, pH = 6), PQ (100 ppm), MB (1.6×10^{-4} M), and R6G (1×10^{-4} M). 0.05 g of amid-p(AN), 400 rpm, room temperature].

k_1 = pseudo-first order rate constant, k_2 = pseudo-second order rate constant.

R^2 = coefficient of determination, q_e = amount adsorbed at equilibrium.

Table III. Amounts of Cd (II), MB, R6G, and PQ in mg/g Adsorbed from Distilled, Tap, River, and Sea Water

Pollutant	Distilled water	Tap water	River water	Sea water
Cd (II)	85.85	131.33	126.97	85.04
MB	90.53	75.37	64.31	22.71
R6G	74.17	28.11	25.79	24.37
PQ	90.58	14.42	6.78	10.56

Reaction conditions; 100 mL solution of Cd (II) (250 ppm, pH = 6), PQ (100 ppm), MB (1.6×10^{-4} M), and R6G (1×10^{-4} M). 0.05 g of amid-p(AN), 400 rpm, room temperature.

The values of q_e and k_2 were calculated from the slope and intercept, respectively, and are given in Table II. As can be seen from Table II, the values of R^2 for the straight lines of pseudo second-order equations are very close to 1, and also the values of q_e calculated from pseudo second-order kinetics are 90.09, 94.34, 95.23, and 78.74 mg/g which are very close to the experimentally observed values of 85.84, 90.57, 90.53, and 74.17 mg/g for the adsorption of Cd (II), PQ, MB, and R6G, respectively. The more suitable values of R^2 and the close resemblance between experimentally observed values and those calculated from pseudo second-order kinetics suggest that the adsorption of Cd (II), PQ, MB, and R6G was abided by pseudo second-order process.

To test the applicability of amid-p(AN) particles in real use, this particle system was also investigated to determine whether it can adsorb organic dyes, herbicide and Cd (II) from different types of water. A 100 mL solution of each of the pollutants was prepared in river, sea, and tap waters. The concentrations of the solutions were kept the same as they were in DI. The amounts of dyes, herbicide and Cd (II) adsorbed per gram of dry amid-p(AN) are given in Table III. Interestingly, a higher amount of Cd (II) can be removed from all types of water as the adsorption capacity of amid-p(AN) from tap water and river water is almost 1.5-fold times more than DI water and sea water, implying that this particle system is very suitable for real applications in the removal of Cd(II) from almost all contaminated environmental aquatic waters.

As the tap and river waters may contain many other metal ions and anions, such as sodium, calcium, magnesium, iron, sulfate, chloride, phosphate, and bicarbonates and so on; some of these anions can give complexes with Cd (II), and/or adhere to the surface of amid-p(AN) beads to promote Cd (II) adsorption by the adsorbent beads. The adhesion of these types of impurities on the surface of beads may provide a new surface for the adsorption of Cd (II), this phenomenon may lead to greater adsorption of Cd (II) from tap and river waters in comparison to pure water. MB can also be removed efficiently from tap, river, and DI; however, the removal from sea water was greatly affected by the presence of various species, such as ions and other contaminants. The removal of R6G and PQ was also affected by the water sources as small amounts were adsorbed from tap, river, and sea water; again due to the presence of naturally soluble ions or added chloride ions in tap water. The

decrease in adsorption capacity of amid-p(AN) particles can be attributed to the presence of different salts that inherently exist and are commonly dissolved in underground water (which is used as tap water), sea water, and river water. These salts are mostly in ionized form in water and the ions produced from these salts may hinder the adsorption capacity of amid-p(AN) particles and hence the adsorption capacity of particles decreased with the exception being for Cd(II) ions. Although the adsorption capacity of the particles was decreased, amid-p(AN) particles can still remove considerable amounts of the three types of pollutants that were studied, i.e., heavy metal ion, organic dyes, and herbicide, from waters with different sources which also contain many interfering species.

CONCLUSIONS

Monodispersed p(AN) particles were prepared by surfactant free emulsion polymerization and the nitrile groups were converted to hydrophilic amidoxime groups. The prepared particles were shown to be good adsorbents for the removal of three different types of pollutants from aqueous media; organic dyes, herbicides, and heavy metal ions. A remarkable increase in the adsorption capacity of amid-p(AN) particles was observed upon amidoximation of nitrile groups. The amid-p(AN) particles were also able to remove all three types of pollutants from waters with different sources: tap, sea, and river. The kinetic studies revealed that these particles can adsorb maximum amounts of the dyes, herbicide, and heavy metal ions within 40 min irrespective of the type of water. Langmuir, Freundlich, and Temkin adsorption isotherms were applied to the adsorption data, and it was found that adsorption of Cd (II) and PQ followed the Langmuir isotherm, whereas MB adsorption followed the Freundlich adsorption model. Pseudo first-order and pseudo second-order kinetics were also applied and the results showed that the adsorption process of Cd (II), PQ, MB, and R6G follow pseudo second-order kinetics more effectively. Interestingly, Cd (II) adsorption capacity of amid-p(AN) particles was found to be very high in tap and river water and almost the same in DI and sea water implying that this amid-p(AN) particle has great potential in the removal of Cd (II) in any kind of contaminated water. Furthermore, this work also reveals that monodispersed p(AN) particles can be prepared without using any surfactant and can be easily chemically modified to amidoximes to increase their adsorption capability for various contaminants with either organic or inorganic sources. Moreover, the p(AN) particles are versatile material as the functional groups on these particles, such as $-\text{COOH}$, and $-\text{NH}_2$, can also be very useful in the removal of a variety of pollutants from waste waters of different sources which also contain many toxic species.

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