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Use of rice straw and radiation-modified maize starch/acrylonitrile in the treatment of wastewater

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Abstract

Graft copolymerization of acrylonitrile onto maize starch by a simultaneous irradiation technique using gamma-rays as the initiator was studied with regard to the various parameters of importance: the monomer-to-maize starch ratio and total dose (kGy). The water absorption of the modified maize starch was measured. The starch modified by acrylonitrile gives low water absorbance. Conversion of the copolymer to the amidoxime form gives high swelling. The gel (%) and the grafting efficiency were measured. An investigation was carried out to study the adsorption of basic violet 7, basic blue 3, direct yellow 50 and acid red 37 from aqueous solutions by the water-insoluble modified starch containing amidoxime groups and rice straw. The effects of initial pH of the solution, pollutant concentration and treatment time on the adsorption were studied and it was found that the maximum adsorption was at 1:2 (starch/acrylonitrile) at irradiation dose 30 kGy.

Keywords: Starch; Rice straw; Radiation; Poly(amidoxime) resin; Dye; Sorption

1. Introduction

The wastewater disposed by textile industries is causing major hazards to the environment and drinking water due to presence of a large number of contaminants like acids, bases, toxic organic, inorganic, dissolved solids and colour. Out of all such contaminants, the colour seems to be the most undesired one, as human eyes can most easily recognize it. It is now a well-established fact that the coloration of water is mainly caused by dyes, which are generally toxic, non-degradable and stable. The stability of dyes towards light and oxidizing agents also create a problem for their removal by different waste treatment procedures. Hence, their removal methods are selected with a great deal of care and thoughtfulness [1]. Formerly, conventional methods adopted by textile industries for removal of coloration from their disposed waste includes, froth flotation, flocculation, etc. However, all such methods were found inefficacious and incompetent. During the last 10 years, the attention has been shifted towards adsorption technique, which has emerged as one of the widely accepted methods for the removal of all such contaminants. The literature survey reveals that a large number of waste products have been utilized as adsorbent, these include peat [2,3] and bagasse fly ash [4,5].

Starch is probably the most abundant and low-cost natural commercially available. Considerable research and technical work have been reported so far, and the chemical modification of starch or modified starch via vinyl graft copolymerization constitutes the most important field for improving the properties of starch, enlarging the range of its utilization [6–12]. Starch graft copolymers can be achieved primarily by free radical initiation process [7,9,11,13]. Emphasis has been placed on high-energy ionization [8,11,12,14]. In this work we attempt to explore the possibility of a new type of grafted starches. Such modified polysaccharides were prepared by grafting acrylonitrile (AN) monomer onto naturally occurring maize starch [15]. The use of the modified polymer for the removal of basic, acid and direct dyes from aqueous solution was studied, which show high adsorption behavior at radiation dose 30 kGy. All articles describing the synthesis of a sorbent with an amidoxime group mostly involve the incorporation of a nitrile group into a polymer matrix, followed by the conversion of the nitrile group into an amidoxime group by treatment with an alkaline solution of hydroxylamine. Various factors affecting the adsorption such as initial pH of the solution, dye concentration, and gel percentage

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of the starch graft copolymers were investigated. Also agriculture by-product such as rice straw will be used in the removal of these dyes from wastewater.

2. Experimental

2.1. Materials

- Maize starch produced by the Cairo Co., for starch and glucose, Egypt.
- Rice straw was supplied by National Research Center, Cairo, Egypt.
- Reagent grade acrylonitrile of purity 98.9% (SD fine, India). Hydroxylamine hydrochloride was used without purification. Other chemicals such as solvents, inorganic salts, acids, etc., were of analytical reagent grade and used as received.
- Dyes: basic violet, basic blue 3, direct yellow 50 and acid red 37.

2.2. Pretreatment of the Fiber

The fibers were soaked in a detergent solution for 30 min, followed by extensive washing with tap water for 1 h and finally with distilled water, and squeezed. The samples were then dried in a drying oven at 40 °C for 4 h then left to dry in air.

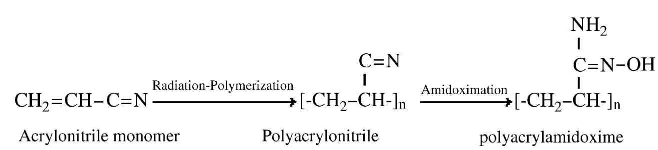
- Alkaline pulping of rice straw:
  Portions of 80 g-depithed rice straw were added to ethanol (50%) as liquor to rice straw ratio of 10:1, then NaOH (2.5%) and anthraquinone (0.1%) were added to the mixture. The mixture was refluxed at temperature of 85 °C for a minimum 3 h. The pulp was extracted and soaked in 1 l cold ethanol (50%) overnight. After this the pulp was washed with cold tap water to complete purity.
- Bleaching:
  The experiment was carried out for rice straw with 4% H_2O_2 in a single stage bleaching process [16] at 105 °C for 60 min.

2.3. Graft copolymerization by simultaneous irradiation

Ten grams of maize starch were mixed with 70 cm^3 of distilled water. The system was stirred at and heated at 85 °C (at the same time for 1 h to form paste-like slurry). The gelatinized starch was cooled at room temperature. A weighed quantity of monomer was added into the gelatinized starch and the total volume is 100 cm^3. The mixture was stirred at 400 rpm at room temperature for 30 min. The gelatinized starch–monomer mixture was transferred into a 20 cm^3 glass and purged with nitrogen gas for 10 min for each tube. It was closed tightly with foil and paraffin film, and then irradiated with gamma rays. The reaction product was dried in oven at 50 °C for 24 h. then irradiation doses of 5, 10, 20, 30, 50, 70, 90 kGy were used to irradiate starch–acrylonitrile mixture. Irradiation of samples was carried out by using a gamma cell (^{60}Co) at dose rate 4.25 kGy h^{-1} (National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority, Egypt).

2.4. Preparation of chelating resin containing amidoxime groups

About 42.1 g of hydroxylamine hydrochloride (NH_2OH, HCl) was dissolved in 300 ml methanolic solution (methanol/water 1:1). The HCl of NH_2OH was neutralized by NaOH solution and the precipitate of hydroxylamine was removed by filtration. The pH of the reaction solution was adjusted to pH 10 by adding NaOH solution. The reaction medium was maintained as methanol to water ratio 1:1. About 20.0 g of grafted starch was placed into the two-neck flask, which was equipped with a mechanical stirrer, condenser and thermostat water bath. Then the above-prepared hydroxylamine solution was added to the flask, and the reaction was carried out at 70 °C and 4 h duration. After completion of the reaction, starch-modified polymer was separated from solution by filtration and washed several times with methanolic solution (methanol/water 1:1). Then, the resin was treated with 200 ml of methanolic 0.1 M HCl solution for at least 5 min. Finally, the resin was filtered and washed several times with methanolic solution (methanol/water 1:1), and then dried at 50 °C [17].



2.5. Modified starch characterization

2.5.1. FT-IR analysis

Infrared spectra of samples were obtained by FT-IR spectrometer (ATI Mattson, Genesis series) USA.

2.5.2. Swelling study of the resin polymer

Dried weights of starch-modified polymer sample were immersed directly in distilled water at room temperature to equilibrium (72 h), after that the swollen polymer was dried at 50 °C to constant weight. The equilibrium degree of swelling (EDS) of the polymer was calculated as

$$\text{content of water absorbed} = \frac{W_e - W_d}{W_d}$$

where W_e is the weight of polymer at the adsorbing equilibrium and W_d is the weight of dried gel after swelling experiment [18].

2.5.3. Gel fraction

The starch-modified polymer samples were put into stainless net of 200 mesh and then the gel was extracted in distilled water at 120 °C for 48 h and then washed by distilled water three times. The remained gel was dried to constant weight at 50 °C. Gel fraction was measured gravimetrically [18]:

$$\text{gel fraction (\%)} = \frac{W_g}{W_0} \times 100$$

where W_g is the weight of dry gel after extraction and W_0 is the initial weight of the dry polymer.

2.5.4. Grafting efficiency (%) (%GE)

%GE was calculated from the increase in weight of starch after grafting in the following manner [19]:

$$\%\mathrm{GE} = \frac{\text{weight of polymer grafted}}{\text{weight of polymer grafted} + \text{weight of homopolymer}} \times 100$$

2.5.5. Scanning electron microscopy (SEM)

The surface topography of the starch-modified polymer and chemically treated rice straw materials were studied by scanning electron microscope of JEOL SEM-25 (Japan). Before the examination the materials were dried, coated with gold under sputter and then observed and photographed.

2.6. Sorption of dyes by batch technique

Dye adsorption from aqueous solution was studied in batch adsorption experiments. The effect of initial pH of the solution, dye concentration, monomer percentage of starch-modified polymer on the adsorption was studied. For batch tests, 0.5 mg of the starch-modified polymer or rice straw was shaken with 50 ml of aqueous dye solutions with a known concentration at room temperature (25 °C) and at different pH values. Blank trials without the addition of the starch-modified polymer or chemically treated rice straw were carried out for each tested pollutant concentration. After the predetermined adsorption time, the polymeric or rice straw adsorbents were separated from the adsorption media, and the analysis for dyes in the aqueous phase were performed using UV–vis spectrophotometer. Freundlich equation [20] was also applied for adsorption of the different dyes onto starch-modified copolymer and chemically treated rice straw. The Freundlich equation is commonly represented as

$$q_e = K_F C_e^{1/n}$$

and the equation may be linearised by taking logarithms as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where q_e is the amount of adsorbate adsorbed on the surface of adsorbent (mg/g), C_e the equilibrium concentration of the adsorbate (mg/l) and K_F and n are Freundlich constants related to amount adsorbed (q, mg/g) and favorability of adsorption, respectively. In general, as the K_F value increases, the amount adsorbed (q, mg/g) of the adsorption for a given dye increases. Values of n show favorable of adsorption of dyes on adsorbent

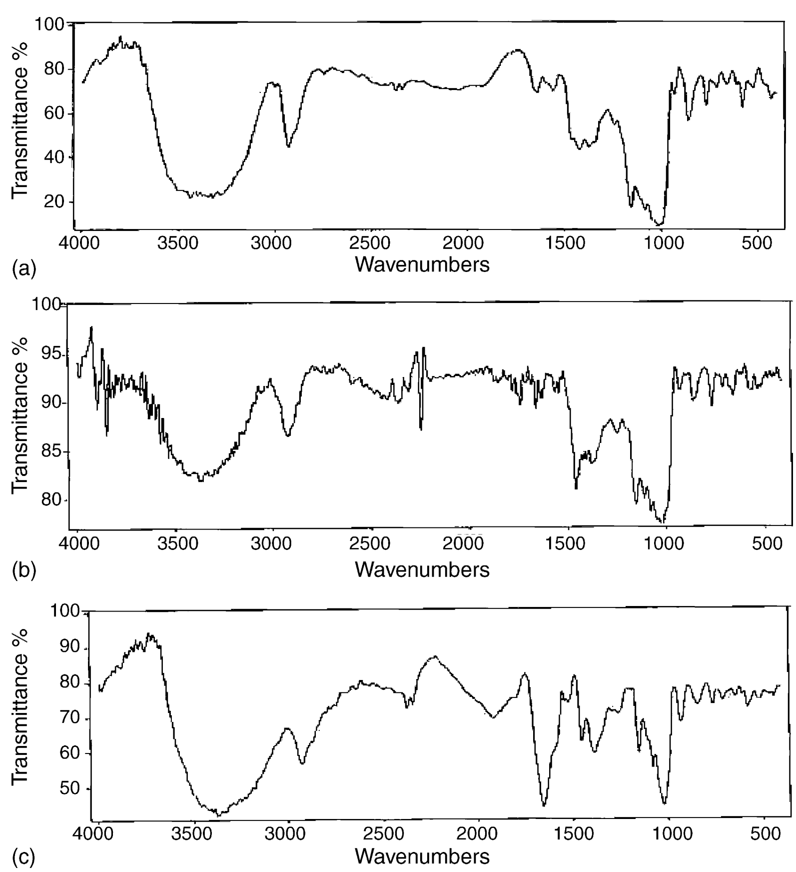


Fig. 1. FT-IR of (a) starch, (b) starch/acrylonitrile and (c) starch/acrylonitrile-amidoxime.

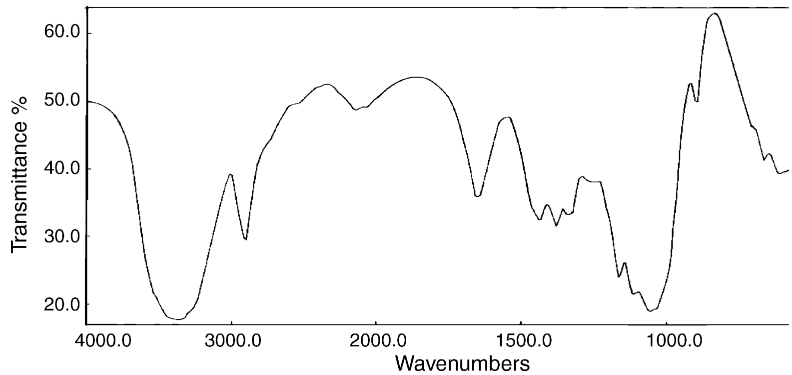


Fig. 2. FT-IR of chemically treated rice straw.

if n values are in between 1 and 10. The plots of log q_e against log C_e give a straight line with the slope and intercept of which corresponds to $1/n$ and log K_F, respectively.

3. Results and discussion

3.1. Characterization of the functional groups of the starch/acrylonitrile copolymer and chemically treated rice straw by FT-IR

The functional groups of the synthesized copolymer were characterized by FT-IR as shown in Fig. 1. The results show that the IR spectra of starch-modified polymer before and after extraction give all the characteristic absorption peaks of maize starch (3423 cm^{-1} (s, broad); 2927 cm^{-1} (m); 1157, 1082 and 1013 cm^{-1} (s) for the O–H, C–H and C–O stretching and bending modes, respectively). Gamma rays produce free radicals at active site of C-2 or C-6 hydroxyl of the starch backbones and the grafting reaction emanates from these sites of the swollen starch to which. FT-IR spectrum of polyacrylonitrile grafted maize starch is presented in Fig. 1(b) the characteristic absorption of polyacrylonitrile at 2245 cm^{-1}due to C≡N stretching modes in addition to same absorption bands of maize starch. After amidoximtion the C≡N band of 2245 cm^{-1} disappeared and formed a new band of amidoxime at 1652 cm^{-1}, and the amid II band of N–H at 1568 cm^{-1}, respectively are shown in Fig. 1(c).

Fig. 2 which illustrated the FT-IR spectrum of chemically treated rice straw shows the infrared of chemically treated rice straw. It was found that, the chemically treated rice straw have a characteristic broad band ranged from 3200 to 3600 cm^{-1}, which corresponds to hydroxyl group of cellulose. The absorption at 2900 cm^{-1} indicates the C–H linkage. Bleached rice straw contained carboxylic acid and hydroxyl functional groups.

3.2. Surface morphology

The surface characteristics of chemically treated rice straw (Fig. 3) and starch-modified polymer (Fig. 4) were investigated by scanning electron microscopy and are presented in Figs. 3 and 4, in order to elucidate the topological changes occurring under radiation modification of starch with acrylonitrile and converting it to the amidoxime structure. The results do not show the difference in the shape of the surface between the blank and after the adsorption of dyes.

3.3. Swelling behavior

In order to analyze the hydrophilic character of the resin produced by irradiation, the properties of water absorption was investigated here. The change in the swelling behavior of resin with the content of starch in the polymeric system and the radiation dose was shown in Figs. 5 and 6. The equilibrium degree of swelling (EDS) of the prepared polymer decreased with the irradiation dose reasonably, and also decreases slightly with the addition of starch and acrylonitrile due to that both starch and acrylonitrile are hydrophobic.

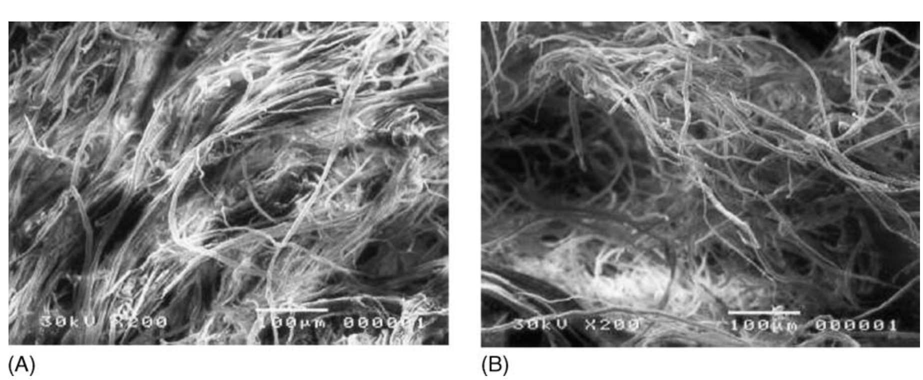


Fig. 3. SEM of (A) chemically treated rice straw and (B) chemically treated rice straw (dye).

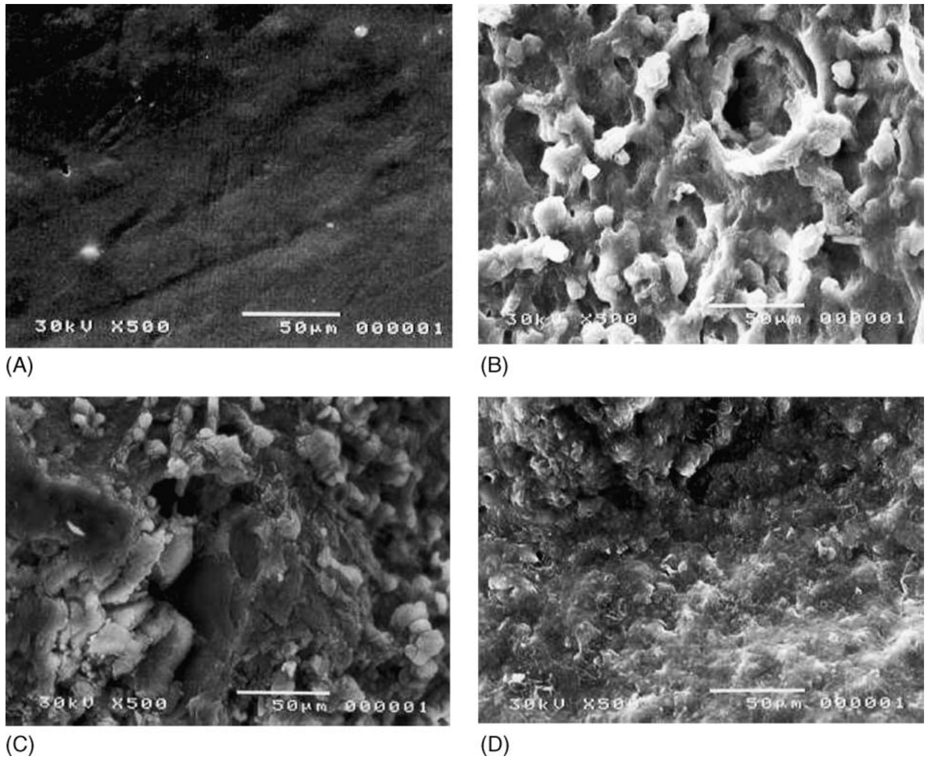


Fig. 4. SEM of (A) blank AN, (B) starch/An (1:2) 3 M, (C) starch/An-oxime, and (D) starch/An-oxime (dye).

3.4. *Gel fraction*

The changes of gel fraction of the prepare polymer with the dose as well as the content of starch in starch-g-AN were shown in Figs. 7 and 8. The gel fraction increased quickly and then leveled off around 30 kGy. But at high dose, gel fraction decreased slightly due to the degradation of the polymer. The gel fraction decreased with increasing of the content of starch in the polymer formed by radiation. The results also showed that the part of starch could not be removed by extraction, i.e. there were two kinds of starch in the modified polymer after irradiation, one was entrapped in the polymer which could be removed easily by extraction, the other could not be removed, was the latter grafted starch in the prepared polymer. Polysaccharides and synthesized polymer blend have been prepared and studied widely, and many researchers thought may be that there was chemical reaction between polysaccharide and synthesized polymer molecules because saccharide groups contain two reactive groups at C_2 and C_3 positions, but up to now no related research was reported [18,21–23]. It can be seen that the gel (%) increases with irradiation time and thereafter it tends to be a curvature relationship. This is due to the behavior and characteristic of free radicals formation in polymers with irradiation time, which in general increases at first then it, tends to level off at higher doses. Meanwhile, the higher the monomer concentration the higher the gel (%) obtained.

3.5. *Grafting efficiency*

Maize starch was modified by incorporating grafting specific polymers to bring about changes in their physical and chemical properties. Radiation-induced grafting of acrylonitrile onto

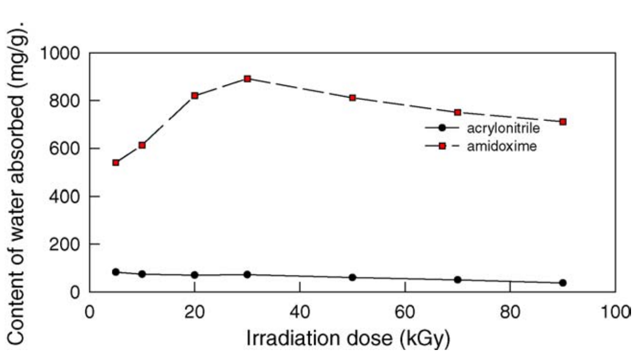


Fig. 5. Effect of total dose on the content of water absorbed (mg/g) of grafted starch with acrylonitrile and the amidoxime.

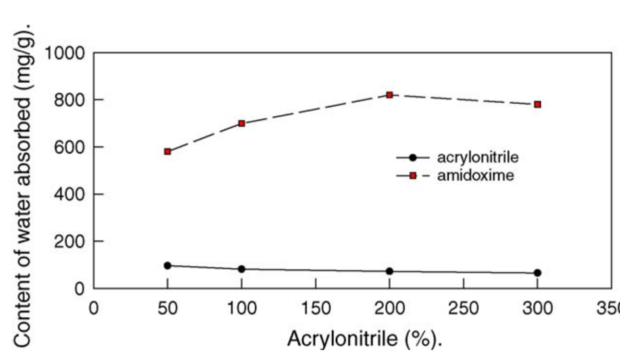


Fig. 6. Effect of acrylonitrile:starch (%) on the content of water absorbed (mg/g) of grafted starch at irradiation dose = 30 kGy.

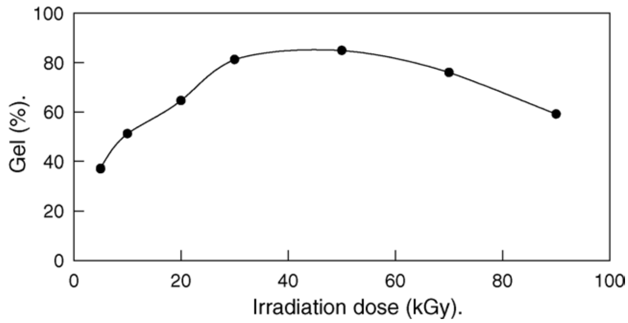


Fig. 7. Effect of total dose on the gel (%) of the grafted corn starch with acrylonitrile.

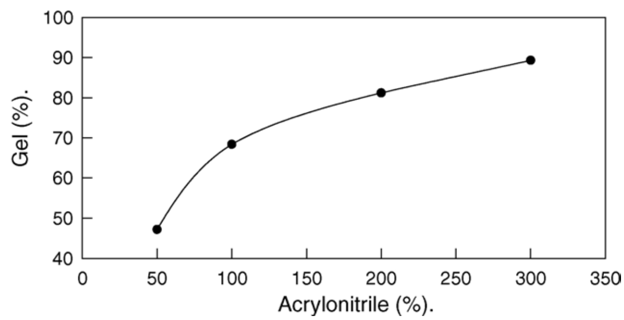


Fig. 8. Effect of the monomer:starch percentage on the gel (%) of the grafted starch at irradiation dose = 30 kGy.

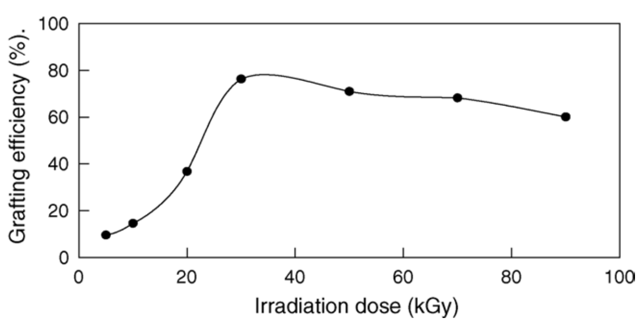


Fig. 9. Effect of total irradiation dose on the grafting efficiency of grafted corn starch with acrylonitrile.

polymeric natural starch, as a convenient way to impart desired properties. The effect of the total dose on the grafting of acrylonitrile (AN) onto maize starch in terms of grafting efficiency is shown in Figs. 9 and 10. Basically, the irradiation dose is

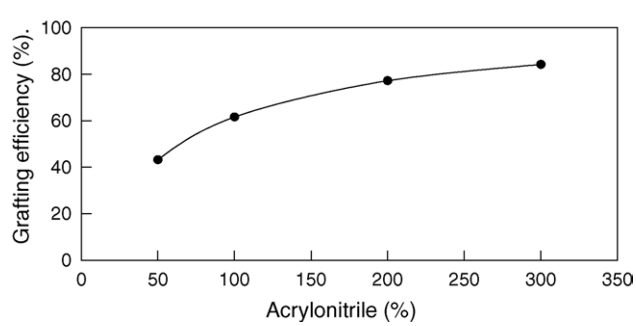


Fig. 10. Effect of the monomer:starch percentage on the grafting efficiency (%) of the grafted starch at irradiation dose = 30 kGy.

an important parameter in any radiation grafting systems. In the direct method, the total dose determines the number of the grafting sites. The percentage conversion increases with increasing total irradiation doses. An increase in the total dose enhances the formation of radicals in the reaction mixture of monomer, starch, and water. All molecules are activated to induce a higher conversion for both homopolymer formation and the grafting reaction. Increasing the total dose reduces the content of the homopolymer and increases the grafting efficiency, because the high total dose can induce ample active grafting sites on the starch backbone for the grafting monomer. However, in the case of graft copolymerization of AN onto starch at the dose rate of 4.25 kGy h^{-1} when the total dose is higher than 30 kGy for AN, the homopolymer content increases and grafting efficiency decreases with increasing total dose. This may be because the higher irradiation dose gives a large amount of radiolysis products (in the absence of oxygen), i.e. $OH^{\bullet}$ and e_{aq}^{-}. This initiates homopolymerization rather than the grafting reaction.

3.6. Studies on sorption of dyes

A well known fact is that the adsorption on a solid takes place in three stages: (a) external diffusion where the mass transfer by diffusion of the absorbate molecules from the bulk fluid phases through a stagnant boundary layer surrounding each adsorbent particle to the external surface of the solid; (b) internal diffusion where the transfer of the adsorbate to the interior of the particle by the migration of the adsorbate molecules from the relative small external surface of the adsorbent to the surface of the pores within each particle; (c) the diffusion of the adsorbate molecules through the pores molecules. The actual adsorption processes where the molecules in the pores are adsorbed from the solution to the solid phase. This later stage is relatively fast, compared to the first two steps, hence local equilibrium usually assumed between these two phases [24].

The role of the adsorbent is very important to the adsorption process as well as the physicochemical characteristics of the adsorbate plays an important role. There was some difference in the magnitude of the efficiency of the adsorption of these pollutants. This difference may be attributed to the difference in molecular size and chemical structure of the dyes. The low adsorbitivity of some of the pollutants onto the different adsorbates may also be due to the steric effects. Many authors found [25–27] that the rate of adsorption of some organic pollutants with side chains showed steric structure effects. The equilibrium adsorption Ce increased with increase in dye concentration. The factors affecting on the affinity of the chemically treated rice straw and modified starch to remove basic violet 7, basic blue 3, direct yellow 50 and acid red 37 from aqueous solutions were studied. This study was carried out to determine the appropriate treatment conditions such degree of grafting and pH at which the removal was performed successfully.

3.6.1. Effect of starch:acrylonitrile-amidoxime ratio on dyes uptake

Fig. 11 shows the relationship between the uptake percent and the starch/acrylonitrile-amidoxime ratio for various dye ions. It

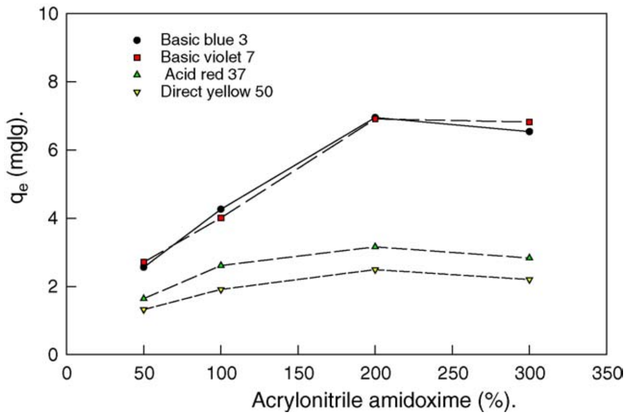


Fig. 11. Effect of acrylonitrile:starch % on the adsorption capacity (mg/g) of starch/acrylonitrile-amidoxime polymer for the different dyes at pH = 7 and initial dye solution conc. = 100 mg/l and time = 8 days.

can be seen that, the uptake of dyes increases as amidoxime amount increases for all dyes. This is due to the increase of the number of functional groups existing in the starch-modified polymer.

3.6.2. *Effect of contact time and pH*

Time needed for the treatment of wastewater dye is an important factor from the economical point of view. Figs. 12–15 shows that, the dye uptake as a function of time for different dyes using starch–acrylonitrile-amidoxime and chemically treated rice straw. Results showed that the dye uptake increases with time to reach its maximum after 8 days. This behavior is observed for all dyes investigated here (basic, acid and direct dyes). To ensure attainment of equilibrium dye uptake, the dyeing was carried out for 10 days. From Figs. 12–15, the adsorbed amount (mg/g) of dye is ordered in the sequence of basic violet 7 > basic blue 3 > acid red 37 > direct yellow 50. The initial rate of adsorbed dye and the maximum value of uptake are very dependent on the structure of dye and the steric effect of the copolymer [28]. The availability of chemically treated rice straw and starch/acrylonitrile-amidoxime materials for dyes was investigated under different pH values in the range from 4 to 10 for all dyes as shown in Table 1. In general, the uptake of anionic dyes (acid and direct dyes) is much higher in acidic solutions than those in neutral and alkaline conditions but the cationic dyes (basic dyes) uptake is higher in alkaline solutions than in neutral and acidic conditions. The adsorption capacities of the anionic dyes onto the starch-modified polymer are much higher than those of the commercial rice straw, at lower pH more protons will be available to protonate amine groups of amidoxime group molecules to form groups $-^{+}NH_3$, thereby increasing electrostatic attractions between negatively charged dye anions and positively charged adsorption sites and causing an increase in dye adsorption. This explanation agrees with our

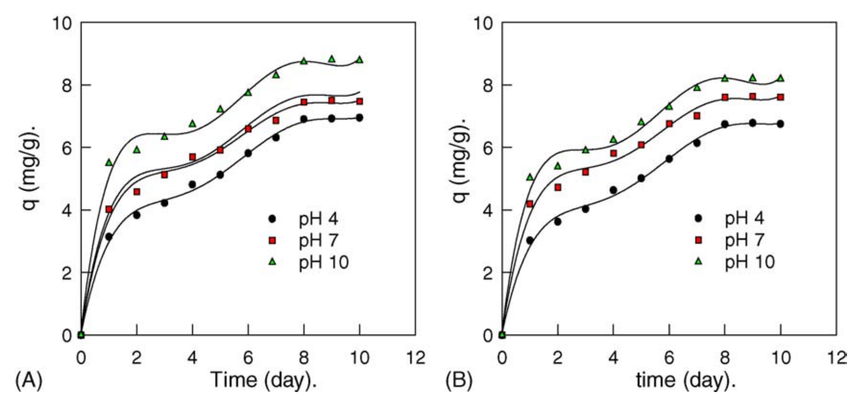


Fig. 12. Effect of time (day) on different dyes uptake (mg/g) for starch–amidoxime, initial conc. = 100 mg/l at different pH values. (A) Basic blue 3 and (B) basic violet 7.

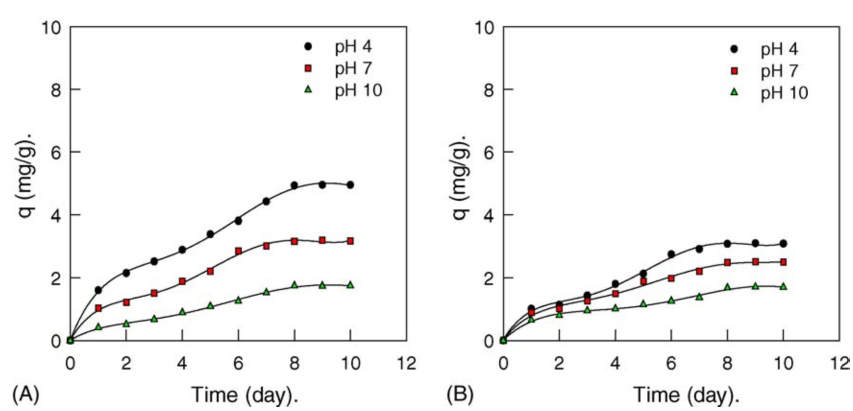


Fig. 13. Effect of time (day) on different dyes uptake (mg/g) for starch–amidoxime, initial conc. = 100 mg/l at different pH values. (A) Acid red 37 and (B) direct yellow 50.

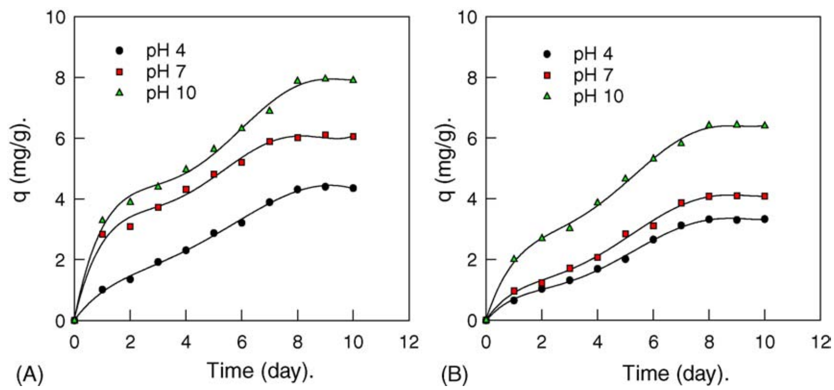


Fig. 14. Effect of treatment time (day) on the different dyes uptake (mg/g) for rice straw, initial conc. = 100 mg/l at different pH values. (A) Basic blue 3 and (B) basic violet 7.

data on pH effect. It can be seen that the pH of aqueous solution plays an important role in the adsorption of direct and acid dyes onto starch-modified polymer. The similar pH effects were also observed by the adsorption of acid dye besides the pH dependence showing the evidence of the electrostatic interaction [29].

The adsorption of basic blue 3 and basic violet 7 dyes is best at pH 10 for both chemically treated rice straw and starch/acrylonitrile-amidoxime materials. This phenomenon is possibly caused by the electrostatic potential between the dye molecule and the lignocellulosic materials surface and the amidoxime group of starch/acrylonitrile-amidoxime. This electrostatic potential can improve the adsorption affinity between dye and chemically treated rice straw and starch/acrylonitrile-amidoxime materials. Thus, the adsorption affinity

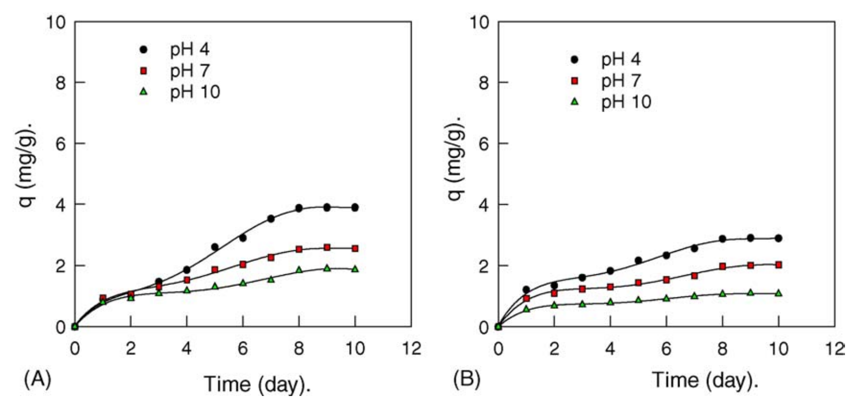


Fig. 15. Effect of treatment time (day) on the different dyes uptake (mg/g) for rice straw, initial conc. = 100 mg/l at different pH values. (A) Acid red 37 and (B) direct yellow 50.

Table 1
Effect of pH on the adsorption of various metal ions (basic violet 7, basic blue 3, direct yellow 50 and acid red 37) on starch/acrylonitrile-amidoxime and chemically treated rice straw; initial dye concentration 100 mg/l and reaction time 8 days

Dye	pH	Amount adsorbed, q_e (mg/g)		
		Starch/acrylonitrile-amidoxime	Blank rice straw	Chemical treated rice straw
Basic violet 7	4	6.4	1.8	3.1
	7	7.3	2.6	4.2
	10	8.3	4.1	6.8
Basic blue 3	4	6.6	2.2	4.1
	7	7.2	3.1	5.5
	10	9.1	4.6	7.8
Direct yellow 50	4	2.8	0.6	2.8
	7	2.1	0.3	1.8
	10	1.2	0.15	1.0
Acid red 37	4	4.8	1.6	3.7
	7	3.1	1.0	2.4
	10	1.6	0.7	1.8

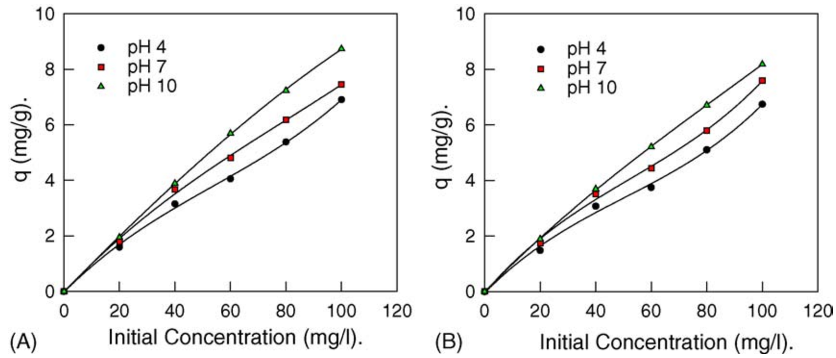


Fig. 16. Effect of initial concentration on the different dyes uptake (mg/g) for starch–amidoxime, at time = 8 days, at different pH values. (A) Basic blue 3 and (B) basic red 7.

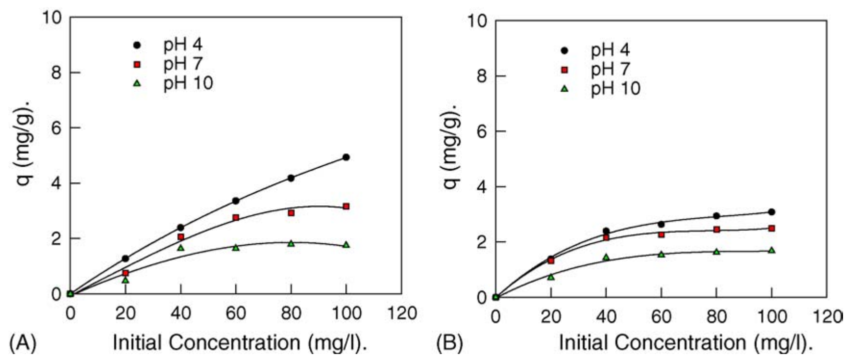


Fig. 17. Effect of initial concentration on the different dyes uptake (mg/g) for starch–amidoxime, at time = 8 days, at different pH values. (A) Acid red 37 and (B) direct yellow 50.

between chemically treated rice straw and starch/acrylonitrile-amidoxime and the basic dyes substrate may increase with the pH of feeding solution and vice versa in the case of acid and direct dyes.

Hwang and Chen [30] reported that both adsorbate and adsorbent might have chemical characteristics that are affected by the concentration of hydrogen ions $[H^+]$ in the solution. Some adsorbents have affinity for $[H^+]$ or $[OH^-]$ ions and can directly affect the solution pH and therefore, the solubility and the amount adsorbed (q, mg/g) may change. Also the presence of the carboxylic −COOH and −OH groups in the adsorbent materials (chemically treated rice straw) affect the amount adsorbed (mg/g). The free carboxylic acid groups present have tendency to form salts with dye cation (basic dye), showing that the affinity between the cationic dye and grafted materials is of chemical nature. The change in dye absorption with increasing pH is due to the number and strength of these weakly acidic groups [31]. Bearing the above-mentioned facts in mind the dye uptake percent increased with the pH of feeding solution, i.e. adsorption increased at very weak $[H^+]$ level. These Starch/acrylonitrile-amidoxime contain a large number of NH_2OH groups and also chemically treated rice straw contain a large number of carboxylic groups that can increase the interaction between the cationic groups of cationic dye and the substrate. While in anionic dyes there was an anionic repulsion between the anionic group of anionic dyes and carboxyl groups in the substrate.

The other type of interaction between the prepared substrate and the cationic dyes may be hydrophobic and hydrogen bond.

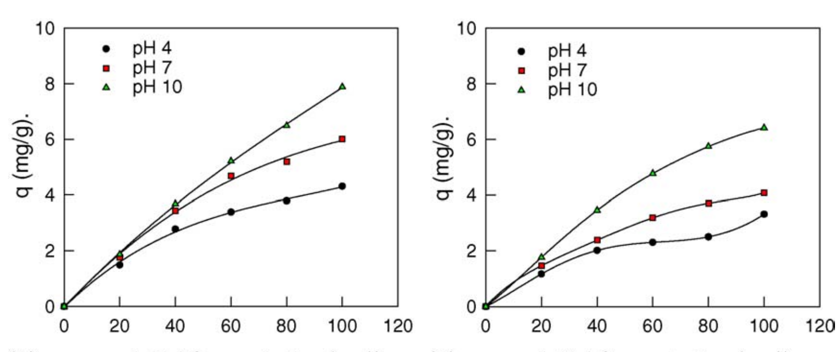


Fig. 18. Effect of initial concentration on the different dyes uptake (mg/g) for rice straw, at time = 8 days, at different pH values. (A) Basic blue 3 and (B) basic red 7.

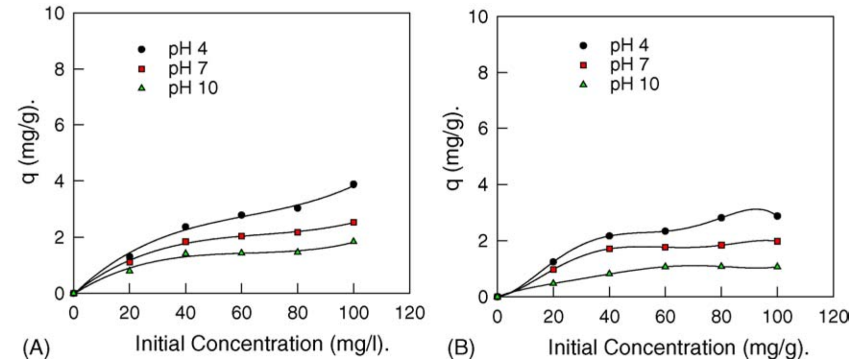


Fig. 19. Effect of initial concentration on the different dyes uptake (mg/g) for rice straw, at time = 8 days, at different pH values. (A) Acid red 37 and (B) direct yellow 50.

Hydrophobic effects were specifically aqueous solutions interactions, which in the present case involve the aromatic rings, the methyl and ethyl groups on the dye molecules. Hydrogen bond will be expected to occur between chemical structure of dye molecules and the resin $(OH)^-$ groups on the monomer units of grafted copolymer. Electrostatic interactions between the dye molecules and the substrate were very dominant due to hydrophobic and hydrogen bonds [32].

3.6.2.1. Effect of initial concentrations. To study the adsorption behavior of these dyes, batch experiment was applied to such system, where dye solution of different concentrations were added to a copolymer or chemically treated rice straw of definite weight after adjustment of their pH values and then were allowed to equilibrate. At the end of this period, the copolymer and chemically treated rice straw showed high adsorption for all dyes as shown in Figs. 16–19 at pH 3, 7 and 10. The removal percent of basic dyes at pH 10 was higher than that at pH 7 and 3, while the removal percent of acid and direct dyes at pH 3 is higher than that at pH 7 and 10. This can be explained by the fact that, in acidic and alkaline medium H^+ protons and OH^- anion become the most predominating species in the medium, which help the charged species of the dyes to interact with the different functional groups of the starch-grafted acrylonitrile-amidoxime copolymer and chemically treated rice straw. It can be seen that the dye uptake initially increases with

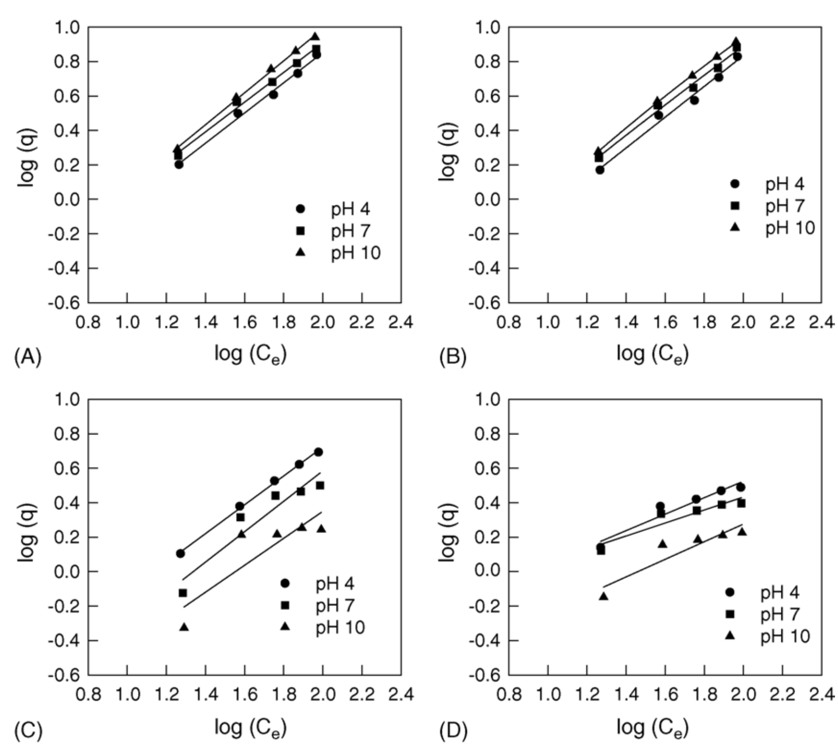


Fig. 20. Relationship between log equilibrium concentration (log C_e) of the different dyes and log (adsorbed amount) by starch/acrylonitrile-amidoxime at different pH values at room temperature. (A) Basic blue 3, (B) basic violet 7, (C) acid red 37, and (D) direct yellow 50.

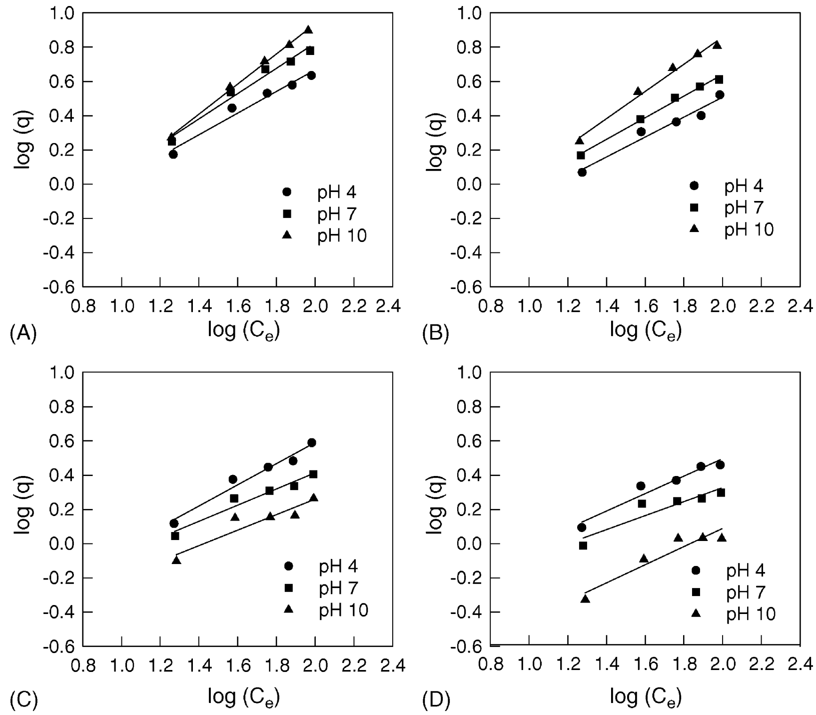


Fig. 21. Relationship between log equilibrium concentration (log C_e) of the different dyes and log (adsorbed amount) by chemically treated rice straw at different pH values at room temperature. (A) Basic blue 3, (B) basic violet 7, (C) acid red 37, and (D) direct yellow 50.

Table 2
The adsorption isotherm parameters (Freundlich constants *k* and *n*) for different adsorbent and different dyes at different pH values at room temperature (25 °C)

	Starch/amidoxime						Chemical treated rice straw					
	pH 4		pH 7		pH 10		pH 4		pH 7		pH 10	
	k	*n*	*k*	*n*	*k*	*n*	*k*	*n*	*k*	*n*	*k*	*n*
Basic blue 3	0.754	1.104	0.749	1.140	0.632	1.028	0.866	1.359	0.813	1.141	0.763	1.079
Basic violet 9	0.578	1.066	0.670	1.099	0.644	1.108	0.806	1.568	0.767	1.528	0.806	1.118
Acid red 37	0.523	1.137	0.337	0.836	0.258	0.876	0.707	1.508	0.703	1.842	0.520	1.929
Direct yellow 50	0.327	1.744	0.659	2.098	0.461	1.444	0.766	1.721	0.687	1.859	0.283	1.342

the feed concentration up to 100 mg/l. This behavior is observed for all types of dyes investigated and also, for different adsorbent materials. Meanwhile, the starch–acrylonitrile-amidoxime possesses higher affinity towards dye than chemically treated rice straw. Also the different in adsorption behavior of such dyes depends mainly on their polarities, initial concentration, molecular structure steric effects as well as their solubilities.

The relationship between log (equilibrium concentration) (log C_e) for the different dyes and log (adsorbed amount) (log q) at different pH values was shown in Figs. 20 and 21 and the adsorption parameters (k and n) was calculated and illustrated in Table 2 for the different adsorbents (starch/acrylonitrile-amidoxime and chemical treated chemically treated rice straw). The numerical values for k show high adsorption affinity of the adsorbents at different pH values. Variation in (k and n) reflects the physico-chemical characteristics of the different dyes on the adsorption process and their affinity for adsorption. In general as the k-value increases, the adsorption capacity of adsorbent for a given compound increases. The slope of the isotherm line may also characterize the adsorption process. Steeper slopes indicate relative good adsorption of the compound when present in high concentration. Slight slopes indicate comparable adsorption over the entire range of concentrations. Consequently, the adsorption parameters (k and n) describe on quantitative basis the adsorption process.

4. Conclusions

The chemically treated rice straw and the prepared copolymer by means of radiation-induced copolymerization of (starch/acrylonitrile) are of interest in some practical uses such as in industrial wastewater treatment and they possessed good hydrophilic properties, which may make them acceptable for practical uses. The dye uptake increased with increasing time up to its maximum value (which is termed here as the equilibrium dye uptake) at almost 8 days of treatment for basic, acid and direct dyes. The NH_2OH-treated ones were imparted dyeability as a result of introduction of amidoxime groups in the polymer structure adsorption ability of the modified polymer was changed with pH of the aqueous solution of dyes. The amounts of adsorption were maximized at pH 10 for the basic dyes and at pH 4 for the direct and acid dyes. Also the radiation-modified polymer gives better results than chemically treated rice straw.

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