



Removal of Heavy Metals and Dyes from Aqueous Medium by using Graft copolymers of Quinoa and Arrowroot Bases

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ABSTRACT: Starch is a storage homo-polysaccharide and is an essential component of the human diet. It is obtained from some of the commercial sources like cereal grains, such as corn, wheat, quinoa, arrowroot, which is a good candidate for industrial exploitation, but, starch has lower mechanical properties, low moisture sensitivity, and have highly biodegradable nature. So for improving the properties of starch, radiation induced graft copolymerization of a binary mixture of acrylic acid and acrylamide on cross-linked arrowroot starch using epichlorohydrin as a crosslinker and on quinoa has been carried out by mutual irradiation technique in the aqueous medium to develop a material with interactive polar functionalities. The grafted copolymers have been characterized by FTIR and SEM methods. The grafted copolymers of cross-linked arrowroot and quinoa starch can efficiently absorb bivalent ions (Ni^{2+} , Cu^{2+} , and Co^{2+}) and Dyes (Malachite Green, Crystal violet, and Congo red) from their respective aqueous solutions. Results show that quinoa based graft and hydrolyzed graft copolymers show best results in dye uptake than arrowroot starch (ARS), whereas, in metal uptake studies, ARS samples show better results than quinoa. Thus, the graft copolymer has been successfully used as a bio-adsorbent for uptaking dyes and metals, thus, saving the water reservoirs.

Keywords: Arrowroot starch, Quinoa, Acrylic acid, Acrylamide, Grafting, Metal ion, Dye uptake

Abbreviations: ARS, arrowroot starch; Qu, quinoa; ECH, epichlorohydrin; AAc, acrylic acid, AAm, acrylamide; FTIR fourier transform infra red spectroscopy; SEM, scanning electron microscopy; CR, congo red; MG, malachite green; CV, crystal violet; Pg, percent grafting; NaOH, sodium hydroxide; HCl, hydrochloric acid.

I. INTRODUCTION

Due to increased population, urbanization, and climate change, the source of fresh water has become limited in the world. Freshwater resources are facing the brunt of environmental pollution by polluting the water resources with industrial effluents, major pollutants organic and inorganic chemicals which include heavy metal ions, industrial and coloured waste from textile mills. In addition, due to industrial effluents, pollution has also intruded the freshwater ecosystems thereby increasing the demand for developing measures for water remediation. Heavy metal ions, Dyes, used in textile industries and other industries like food, paper, carpet, rubber, plastics and cosmetics are the waste in natural streams that increase the toxicity and Chemical Oxygen Demand (COD) and also reduce light penetration, which has a critical effect on photosynthesis. The use of natural polymers in the removal of pollutants from wastewater has become important due to their biodegradable behaviour.

Natural polymers can be chemically tailored to such materials that they can absorb and hold a large amount of water within their three-dimensional network structure [1]. The three-dimensional network structure can be attained through cross-linking, which provide interactive

functional properties. Pourjavadi *et al.*, [2] carried out radical copolymerization of acrylate starch with AAc and AAm using initiator ammonium persulphate in aqueous solution to yield hydrogels and found that AAm grafted hydrogel has a well-built network than AAc grafted hydrogels. Reddy and Yang (2010) synthesized citric acid-*c*-starch with better strength, thermal stability and due to this dissolution of starch films decreased in water and formic acid [3]. Bardajee *et al.*, (2010) prepared new novel, smart biopolymer by using radiochemical methods for cross-linking and graft copolymerization of AAc onto Salep backbones and prepared superabsorbent hydrogel [4]. Different effluents in water are highly undesirable and unsafe to use. Many physicochemical methods have been tested for treating waste water but adsorption has been considered to be the superior one. Cross-linked carboxymethyl starch in the ionized form was used for the elimination of metal ions (Cu^{2+} , Pb^{2+} , Cd^{2+} , Hg^{2+}) from their respective aqueous solutions. Igura and Okazaki (2012) used phosphorylated sago starch-extraction residue for the removing heavy metal ions from water [5]. Feng and Wen (2017) prepared potato starch xanthate through cross-linking that can efficiently absorb metal ions (Pb^{2+} and Cd^{2+}) and investigated their absorbency [6]. Sancey *et al.*, (2011) used cross-linked starch in surface

treatment plant where discharge coming out from industry was collected and found it to exhibit high sorption affinity for metal and fluoride ions [7]. Koriche *et al.*, (2012) developed cationic-starch/clay bionano-composites and utilized for the removal of congo red dye [8]. Nsom *et al.*, (2019) synthesized Pectin-starch magnetite hybrid nanoparticles with the iron salt and observed them as good absorbents for dye (methylene blue) for purifying waste water of the textile industry [9]. Soto *et al.*, (2016) synthesized Hydrogels of itaconic acid onto corn starch by free radical graft copolymerization using potassium permanganate and sodium bisulfite as redox initiation system [10]. Tekade *et al.*, (2020) modified arrowroot & corn starch as an environmentally friendly adhesive product [11]. The purpose of the current study is to prepare graft copolymers via cross linking of natural product Arrowroot with epichlorohydrin and Quinoa by using a mixture of acrylate monomers (Acrylamide and acrylic acid). Furthermore, optimum samples were used as bio absorbent for the removal of acidic and basic dyes, and metal ions uptake studies.

II. MATERIALS AND METHODS

Arrowroot starch (ARS) and quinoa (Qu), were purchased in the form of seeds/grains, epichlorohydrin (ECH) (Acrös Organics) was used as a cross-linking agent; acrylic acid (AAc) and acrylamide (AAM) (E. Merck) as monomers, anhydrous sodium sulfate, NaOH and HCl (S.D Fine Chem. Ltd. Mumbai) were used as such and distilled water was used as reaction medium. Quinoa seeds were crushed to powder before use.

A. Preparation of cross-linked ARS (ECH-cl-ARS)

Arrowroot starch (1.0g) was suspended in 5 mL of water and to it anhyd. sodium sulfate (0.05g) was added. The reaction mixture was stirred to prepare slurry and its pH was adjusted to 11 by the addition of 3% aqueous NaOH solution. The reaction mixture was transferred to a standard tri-necked round bottomed flask, fitted with a water condenser, thermometer and separating funnel. The flask was placed on the rota mantle maintained at a constant temperature (40°C) and epichlorohydrin (5mL) was added dropwise from the separating funnel. After the designated time period, the starch slurry was brought to pH 5.25±0.25 using HCl (3%) solution and filtered. The cross-linked starch and ECH-cl-ARS was then washed three times with water, air-dried overnight at 30°C.

B. Graft Copolymerization

The graft copolymers of ECH-cl-ARS and quinoa have been prepared by the mutual radiation method. Weighed ECH-cl-ARS / quinoa (1.0g) was suspended in 1.5 mL of water in a test tube, then known amount of binary monomers, (AAc+AAM) were added, taken in definite proportions. The mixture was stirred for 3-4min to prepare a thick suspension. The thick suspension so obtained was irradiated in Gamma chamber for 24 h at a constant dose rate of 0.22 kGy/ h. After the specified time period, the reaction mixture was removed from the Gamma chamber and the respective graft copolymers, (ECH-cl-ARS)-g-poly(AAc-co-AAM) and Qu-g-poly(AAc-co-AAM), obtained as monoliths, were removed from the test tube. After extensive washings with water, the graft copolymers were then dried in the oven and weighed. The Pg was calculated from the increased weight of the cross-linked copolymer upon grafting as follows:

$$\text{Percentage of grafting (Pg)} = \left(\frac{W_g - W_o}{W_o} \times 100 \right)$$

Where W_o and W_g , are respectively the weights of pristine, cross-linked arrowroot starch, quinoa and the respective graft copolymers.

C. Procedure for Dye Uptake Studies

Basic dyes, malachite green (MG) and crystal violet (CV) and acid dye, congo red (CR) were used for dye uptake studies by pristine ARS and pristine quinoa, pristine cross-linked starch, ECH-cl-ARS, grafted copolymers, (ECH-cl-ARS)-g-poly(AAc-co-AAM), and Qu-g-poly(AAc-co-AAM) and the hydrolyzed samples. Standard curves for all the dyes CV, MG and CR were drawn by plotting OD (measured at λ_{max} 591 nm, 637nm and 498nm respectively) versus concentrations of the dye solution. The weighed samples were placed in 50 mL of aqueous solution separately; in the respective dye solution (0.0125%) for different time periods at room temperature. The optical density of the residual dye solution after each specified time of immersion was noted. After the maximum immersion time of 72h, the samples were removed from the aqueous dye solution and then dried. The percentage of dye uptake was calculated by using the following expression:

$$\text{Percent Dye uptake} = \frac{C_i - C_R}{C_i} \times 100$$

here C_i is the initial concentration of dye solution and C_R is the concentration of the residual dye solution, determined from the standard curve.

D. Procedure for Metal Uptake Studies

Percent metal uptake (Co^{2+} , Cu^{2+} , Ni^{2+}) of hydrolyzed graft copolymers of ARS, (ECH-cl-ARS)-g-poly (AAc-co-AAM) and quinoa, Qu-g-poly (AAc-co-AAM) as adsorbents for metal uptake has been investigated. Percent metal uptake has been studied as the function of time and the concentration of the total uptake of metal by the polymer samples has been determined from the standard curves of Co^{2+} , Cu^{2+} , Ni^{2+} ion solutions by plotting different ion concentrations against OD (measured at λ_{max} 394, 229 and 512 nm) respectively.

III. RESULTS AND DISCUSSION

Effect of reaction conditions of grafting of (AAM+AAc) onto ECH-cl-ARS and Quinoa:

Percentage grafting (Pg) of a binary monomer mixture of (AAc + AAM) on ECH-cl-ARS and quinoa was studied as the function of various reaction parameters such as monomer concentration and total dose and results are shown in Table 1.

Keeping the amount of AAc fixed (2.77 mol/L), the concentration of AAM was varied and the Table shows that Pg of the binary monomer mixture, (AAc + AAM), onto cross-linked ARS initially decreases with increasing concentration of acrylamide and then increases. Maximum grafting (240%) was obtained at [AAM] = 1.40 mol/L. Taking [AAM]=1.40 mol/L as the optimum, acrylic acid concentration in the binary mixture was varied and the Table shows that Pg of the cross-linked starch increase with higher [AAc] showing maximum grafting of (240%) using 2.77 mol/L of AAc beyond which it decreases. Upon varying the total dose, i.e. time of irradiation, Pg of the binary monomer mixture on both the polymeric backbone decreases with increasing total dose showing maximum grafting of (240%) at a 28.51 kGy of the total dose.

When the effect of reaction conditions on Pg of the binary monomer mixture (AAc + AAm) was studied, onto quinoa, it is observed from the Table that on varying the concentration of AAm and AAc percent grafting shows a decrease and then an increase with increasing [AAm] while it shows an increase in Pg with increasing [AAc]

giving maximum grafting percentage of 90% using respectively 0.35 mol/L and 2.77 mol/L of AAm and AAc. While varying total dose, percent grafting of the binary monomer mixture decreases with increasing total dose. Maximum Pg (90 %) was obtained at a 28.51kGy of the total dose.

Table 1: Effect of Total dose and [AAc], [AAm] on Percentage of Grafting of (AAc+AAm) onto ECH-*c*-ARS and Quinoa.

S. No.		[AAm] mol/L	[AAc] mol/L	Total dose (kGy)	% Grafting
1.	ARS	0.35	2.77	28.51	216.00
2.		0.70	2.77	28.51	210.00
3.		1.40	2.77	28.51	240.00
4.		2.11	2.77	28.51	184.00
5.		0.35	2.77	35.64	38.00
6.		0.35	2.77	48.70	16.00
7.		0.35	2.77	56.02	40.00
8.		0.35	1.38	28.51	6.00
9.		0.35	4.16	28.51	68.00
10.	Qu	0.35	—	28.51	60
11.		—	0.70	28.51	54
12.		0.35	2.77	28.51	90
13.		0.35	2.77	35.64	46
14.		0.70	2.77	35.64	60
15.		1.05	2.77	35.64	68
16.		0.35	1.38	35.64	82
17.		0.35	4.16	35.64	90
18.		0.35	2.77	48.70	56
19.		0.35	2.77	56.02	52

The decrease in Pg with increasing monomer concentration (both AAm and AAc) and the total dose is attributed to the fact that both the factors promote homopolymer /copolymer formation at the values beyond the optimum values in preference to the grafting thus lowering grafting percentage.

Characterization

(i) **FTIR Spectroscopy:** For recognizing the physicochemical structure of the samples, FTIR spectroscopic analysis was carried out on Thermal 5700 spectrophotometer. FTIR spectra of pristine arrowroot starch, cross linked arrowroot starch, ECH-*c*-ARS, grafted arrowroot starch, (ECH-*c*-ARS)-g-poly (AAc-co-AAm), pristine quinoa, Qu-g-poly (AAc-co-AAm) and the respective hydrolyzed graft copolymers are shown in Figs.1 and 2. The pristine arrowroot starch (Fig. 1a) and pristine quinoa (Fig. 2a) shows broad peaks between

3600-3200 cm^{-1} , 2931.2 - 2650 cm^{-1} and between 1158.7-1149 cm^{-1} respectively due to associated hydroxyl groups ($\nu_{\text{O-H}}$ str), $\nu_{\text{C-H}}$ str, and $\nu_{\text{C-O-C}}$ str. In the cross-linked ARS (Fig. 1b), the peak due to $\nu_{\text{O-H}}$ str is less broad than the pristine starch (3315.78 cm^{-1} & 3388.1 cm^{-1} respectively) indicating that cross-linking has taken place that affects the association of hydroxyl groups. The spectra of the grafted samples (ECH-*c*-ARS)-g-poly(AAc-co-AAm) (Fig.1c) and Qu-g-poly(AAc-co-AAm) (Fig. 2b), in addition to the peaks of pristine cross-linked starch, ECH-*c*-ARS and pristine quinoa, show additional sharp peaks at 1731 cm^{-1} , 1720 cm^{-1} and 1720 cm^{-1} due to $\nu_{\text{C=O}}$ str of the carboxylic groups and the peaks at 1673 cm^{-1} , 1548.1 cm^{-1} ; 1651 cm^{-1} , 1557 cm^{-1} ; and 1600 cm^{-1} , 1520 cm^{-1} due to $\nu_{\text{C-O}}$ str and $\nu_{\text{N-H}}$ bending of the carboxylic and amide groups of the grafted poly (AAc-co-AAm) chains respectively.

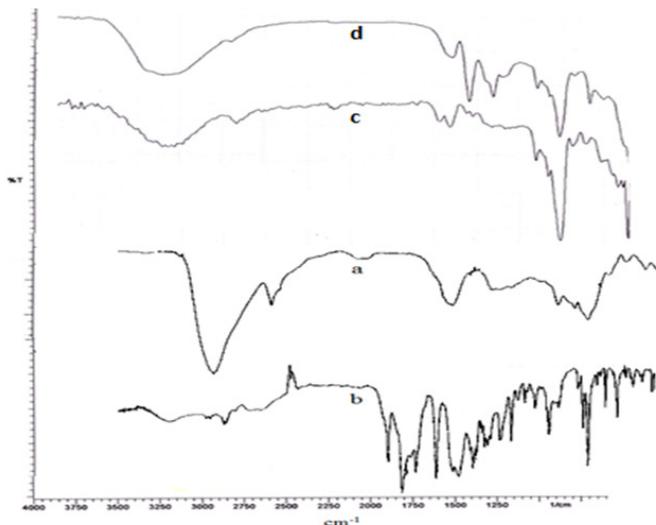


Fig. 1. FTIR Spectra of (a) Pristine Arrowroot Starch, (b) (ECH-*c*-ARS), (c) (ECH-*c*-ARS)-g-poly(AAc-co-AAm), (d) hydrolyzed (ECH-*c*-ARS)-g-poly (AAc-co-AAm).

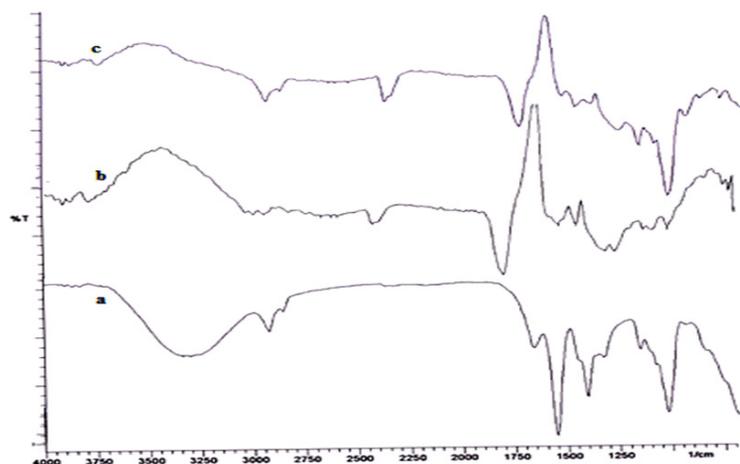


Fig. 2. FTIR Spectra of (a) Pristine Quinoa (b) Qu-g-poly(AAc-co-AAm) (c) hydrolyzed Qu-g-poly (AAc-co-AAm).

In the IR spectra of the respective hydrolyzed samples (Figs. 1d&2c) except for the shift of the peak due to $\nu_{C=O}$ str of the carboxylic groups to a lower value 1690-1650 cm^{-1} due to the carboxylate ion, all others peaks are observed. IR spectral data, is thus, evidence of successful cross-linking, grafting of a binary mixture, (AAc+AAm) and hydrolysis of graft copolymers has been successfully achieved.

(iii) Scanning Electron Microscopy: Surface modification of pristine ARS and pristine quinoa and other samples were studied by Scanning Electron Microscopy on SEM QUANTA 250 D 9393 model. Scanning electron microscopy pictures of pristine arrowroot starch, cross linked arrowroot starch, ECH-*cl*-ARS grafted arrowroot starch, (ECH-*cl*-ARS)-g-poly (AAc-co-AAm), hydrolyzed grafted arrowroot starch; pristine quinoa, grafted quinoa, Qu-g-poly (AAc-co-AAm) and hydrolyzed grafted quinoa were recorded to

gain insights of the morphology of the polymers and the copolymers. The SEM of pristine arrowroot starch and quinoa shows a granular structure (Figs. 3a&4a) respectively. The surface of ARS is disrupted after cross-linking. It exhibits a slightly rough surface with some black zones (Fig. 3b). While investigating the surface morphology of grafted copolymers, (Figs. 3 c & 4 b respectively), it is observed that graft copolymers (ECH-*cl*-ARS)-g-poly(AAc-co-AAm) and Qu-g-poly(AAc-co-AAm) show a heterogeneous loose surface in comparison to pristine and cross-linked due to the formation of the grafts on the surface of the polymers. Scanning electron microscopy (Figs. 3d&4c) of the hydrolyzed grafted copolymers, ARS and quinoa present similar surface topology as that of the grafted samples with a difference of appearance of spaces between the polymer grafted surfaces.

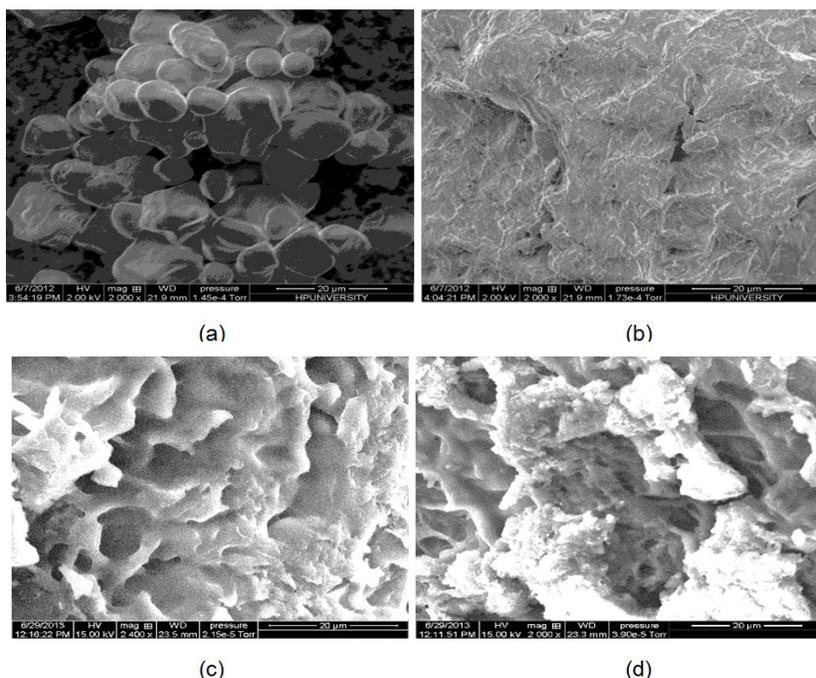


Fig. 3. SEM of (a) Pristine ARS (b) ECH-*cl*-ARS (c) (ECH-*cl*-ARS)-g-poly (AAc-co-AAm) (d) hydrolyzed (ECH-*cl*-ARS)-g-poly (AAc-co-AAm).

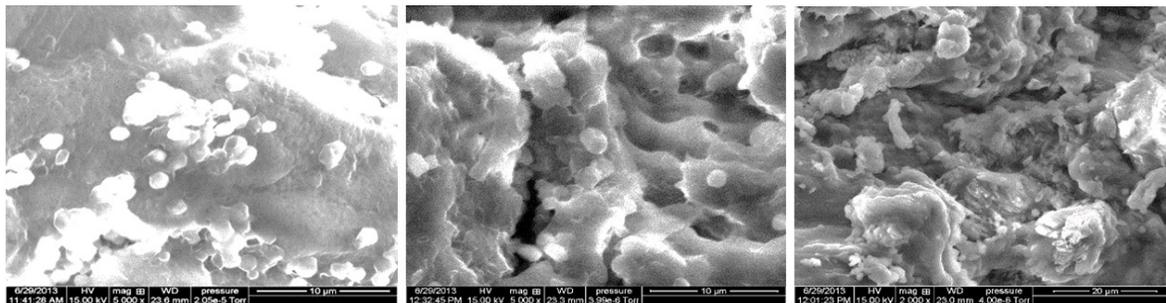


Fig. 4. SEM of (a) Pristine Quinoa (b) Qu-g-poly (AAc-co-AAm) (c) hydrolyzed Qu-g-poly (AAc-co-AAm).

The change in the surface morphology of the pristine polymers upon cross-linking and grafting evinces successful cross-linking and grafting processes.

Dye Uptake Studies: The graft copolymer obtained during grafting reaction shows different swelling ability which would be expected to have varied absorbency for the dyes [12] and bivalent metal ions [13] at room temperature as a function of time. Therefore, in the present study, the starch based graft and hydrolysed copolymers have been utilized for the uptake of basic dyes (Crystal Violet and Malachite Green) and acidic dye (Congo red) from their respective aqueous solutions. Percent dye uptake was evaluated by determining the decrease in optical density of the residual solutions of the respective dyes at 591nm, 637nm and 498nm respectively. The concentration of the total dye adsorbed by the polymer samples was determined from the standard curves of CV, MG, and CR dye solution by plotting different dye concentrations against optical densities (Figs. 5-7).

The percent dye uptake by pristine arrowroot starch, ECH-*cl*-ARS, (ECH-*cl*-ARS)-g-poly (AAc-co-AAm), pristine quinoa and Qu-g-poly (AAc-co-AAm) and the respective hydrolyzed grafted samples have been studied as a function of time and the results are

presented in Figs. 8-13. In case of CV (Figs. 8 & 11), percent dye uptake by pristine and cross-linked, grafted and hydrolyzed grafted samples of ARS and quinoa respectively, it is observed from the figures that the ARS samples show the maximum dye uptake for the hydrolyzed grafted ARS (94.49% in 24h) followed by cross-linked ARS (76.08% in 48h), grafted ARS (37.40% in 24h) and least for the pristine ARS (2.43% in 3h).

When quinoa samples are used as adsorbents, maximum dye uptake is observed for the hydrolyzed grafted samples (93.09% in 24h) followed by pristine quinoa (7.79% in 48h) and the least by the grafted quinoa samples (3.47% in 72h).

When the respective samples were used as an adsorbent for Malachite Green (MG) (Figs. 9 & 12), maximum dye uptake by the ARS samples is observed for the grafted ARS sample (92.89% in 24h) followed by hydrolyzed grafted ARS sample (70.02% in 24h) and ECH-*cl*-ARS (58.88% in 48h) with pristine ARS showing minimum affinity (21.14% in 24h). Quinoa shows maximum dye uptake for the hydrolyzed grafted samples (96.89% in 48h) followed by grafted quinoa samples (75.60% in 24h) and the pristine quinoa (7.29% 2h) showing the minimum affinity for the MG dye.

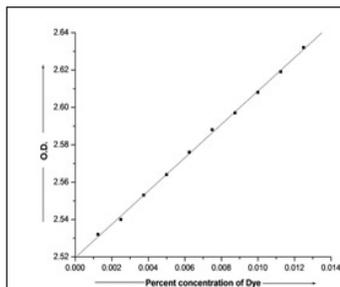


Fig. 5. Standard curve for CV.

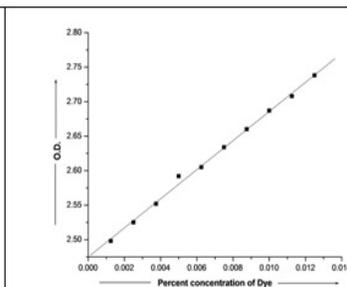


Fig. 6. Standard curve for MG.

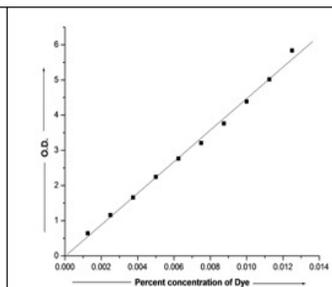


Fig. 7. Standard curve for CR.

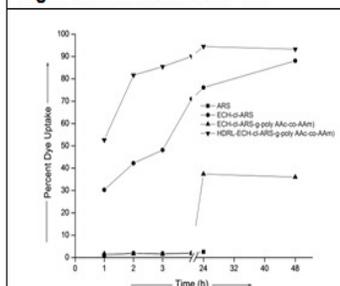


Fig. 8. Percent dye Uptake of CV Dye as a function of contact time in ARS.

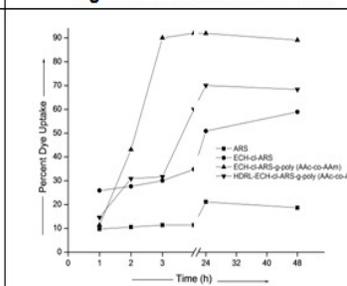


Fig. 9. Percent dye Uptake of MG Dye as a function of contact time in ARS.

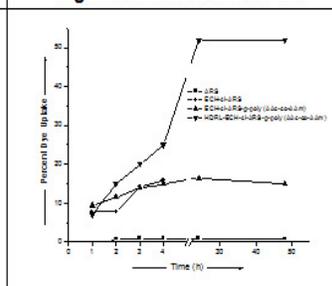


Fig. 10. Percent dye Uptake of CR Dye as a function of contact time in ARS.

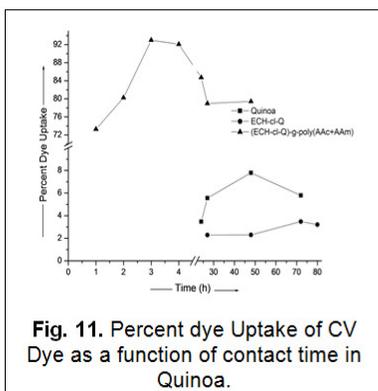


Fig. 11. Percent dye Uptake of CV Dye as a function of contact time in Quinoa.

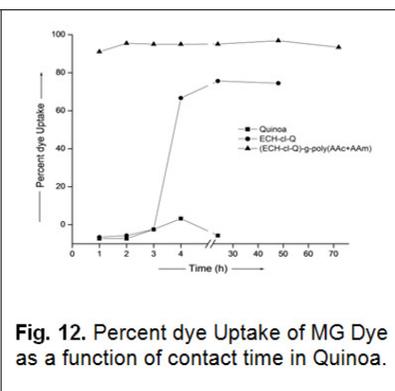


Fig. 12. Percent dye Uptake of MG Dye as a function of contact time in Quinoa.

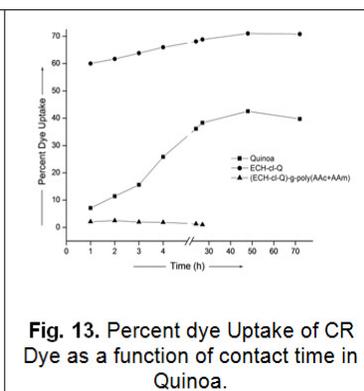


Fig. 13. Percent dye Uptake of CR Dye as a function of contact time in Quinoa.

In case of the dye uptake of the anionic dye (CR) (Figs. 10 & 13), it is observed from the figure that the ARS hydrolyzed grafted copolymer shows a continuous increase in percent dye uptake giving maximum (52.00% in 24h) followed by grafted ARS (16.32% in 4h) and then cross-linked and pristine ARS (15.80% in 4h & 2.12% in 1h respectively), while the quinoa grafted show maximum percent dye uptake of 71.03% in 48h followed by pristine Qu (42.55% in 48h) and least by the hydrolyzed grafted quinoa (2.49% in 2h).

From overall data of the dye uptake studies, depending on the maximum percent dye uptake, following order of the polymer substrates towards maximum dye adsorption has been observed for CV, MG and CR:

CV hydrolyzed grafted (ECH-cl-ARS)-g-poly (AAc-co-AAm) (94.49%) > ECH-cl-ARS (76.08%) > (ECH-cl-ARS)-g-poly (AAc-co-AAm) (37.40%) > ARS (2.43%).

CV hydrolyzed grafted Qu-g-poly (AAc-co-AAm) (93.09%) > Qu (7.79%) > Qu-g-poly (AAc-co-AAm) (3.47%).

MG (ECH-cl-ARS)-g-poly (AAc-co-AAm) (92.89%) > hydrolyzed grafted (ECH-cl-ARS)-g-poly (AAc-co-AAm) (70.02%) > ECH-cl-ARS (58.88%) > ARS (21.14%).

MG hydrolyzed grafted Qu-g-poly (AAc-co-AAm) (96.89%) > Qu-g-poly (AAc-co-AAm) (75.60%) > Qu (7.29%).

CR hydrolyzed grafted (ECH-cl-ARS)-g-poly (AAc-co-AAm) (52.00%) > (ECH-cl-ARS)-g-poly (AAc-co-AAm) (16.32%) > ECH-cl-CS (15.80%) > ARS (2.12%).

CR Qu-g-poly (AAc-co-AAm) (71.03%) > Qu (42.55%) > hydrolyzed grafted Qu-g-poly (AAc-co-AAm) (2.49%).

From the results it is, thus, observed that the grafted and the hydrolyzed grafted samples of ARS and quinoa show promising results as an adsorbent for both anionic and cationic dyes. From among the two starch backbones, quinoa gives excellent results for the three dyes as compared to ARS.

Metal Ion Uptake Studies

Percent metal uptake (Ni^{2+} , Co^{2+} , Cu^{2+}) [14,15] by the hydrolyzed graft copolymers, (ECH-cl-ARS)-g-poly (AAc-co-AAm) and Qu-g-poly (AAc-co-AAm) as adsorbents for the metal uptake has been investigated as the function of time and the results are shown in Table 2. The concentration of the total metal uptake by the polymer samples were determined from the standard curves of Ni^{2+} , Co^{2+} , Cu^{2+} ion (Figs. 14-16 respectively) solutions by plotting different ion concentrations against OD (measured at λ_{max} 512nm, 229nm and 394nm).

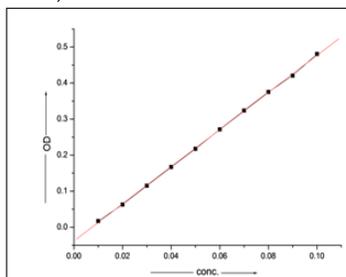


Fig. 14. Standard curve for Ni^{2+} .

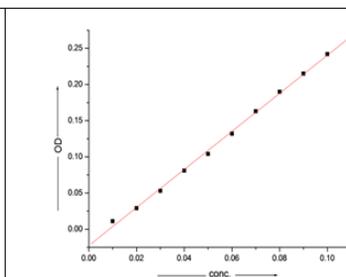


Fig. 15. Standard curve for Cu^{2+} .

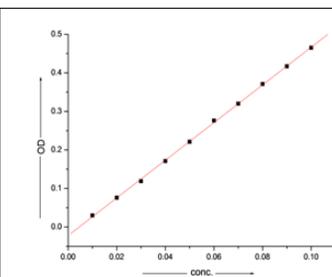


Fig. 16. Standard curve for Co^{2+} .

Table 2: Percent Metal Ions uptake by the Hydrolyzed Graft Copolymers of Arrowroot and quinoa Starch.

S. No.	Hydrolyzed Sample	Metal Ion	% uptake					
			1h	2h	3h	4h	24h	48h
1.	(ECH-cl-ARS)-g-poly(AAc-co-AAm)	Cu^{2+}	1.01	1.02	1.30	1.50	3.82	—
2.		Co^{2+}	37.7	38.3	39.4	36.1	1.14	—
3.		Ni^{2+}	27.92	28.2	28.8	25.4	12.1	—
4.	Qu-g-poly(AAc-co-AAm)	Cu^{2+}	0.20	0.99	0.39	1.70	2.01	0.70
5.		Co^{2+}	5.27	7.03	2.21	2.64	1.64	—
6.		Ni^{2+}	8.14	9.92	4.59	1.05	1.63	—

The table shows that the hydrolyzed grafted samples of ARS and quinoa show a low affinity for the metals. Hydrolyzed grafted ARS sample also show a better affinity for Co^{2+} with 39.4% in 3h and 28.8% in 3h for Ni^{2+} but the lesser affinity for Cu^{2+} i.e. 3.82% in 24 h. On the other hand, hydrolyzed grafted quinoa shows the minimum metal uptake as compared to other AR starch, maximum uptake is for Ni^{2+} (9.92% in 2h) followed by 7.03% in 2h for Co^{2+} and 2.01% in 24h for Cu^{2+} .

IV. CONCLUSION

From the foregoing discussion, it is thus evinced that arrowroot starch has been successfully cross-linked. Radio-chemical graft copolymerization of the binary monomer mixture of hydrophilic acrylic acid and acrylamide on the cross-linked ARS and quinoa has been successfully carried out. Base catalyzed hydrolysis of the grafted copolymers was also carried out and the hydrolyzed grafted copolymers show excellent swelling behaviour to that of the grafted copolymers. The structure of graft and the hydrolyzed graft copolymers has been characterized by FTIR and Scanning electron microscopic methods. The graft copolymers have been successfully used as a bio- absorbent for the removal of both acidic and basic dyes, bivalent metal ions, thus, saving the water reservoirs against pollutants.

Based on dye uptake studies it was observed that Quinoa based graft and hydrolyzed graft copolymers show best results in comparison to those of ARS, But in Metal uptake studies, discussed above it was observed that ARS based hydrolyzed graft copolymers show best results in comparison to those of quinoa samples.

V. FUTURE SCOPE

Different experimentation can be done by the starch bases in flocculation studies for water turbidity removal coming out from industrial waste. These bases used for making the starch-based biodegradable film which can be used in agriculture for the growth of the plant.

Conflict of Interest. The author declares no conflict of interest.

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