Fabrication and Characterization of Amidoxime-Grafted Silica Composite Particles *via* Emulsion Graft Polymerization

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ABSTRACT: *This study deals with the synthesis and characterization of polyacrylonitrile (PAN)-grafted silica composite particles by emulsion graft polymerization using potassium persulphate as the initiator and Tween 80 as the surfactant for potential application in wastewater treatment. The commercially available silica particles (35-70 micron) were first functionalized with vinyltriethoxysilane that were subsequently employed for the grafting of PAN via emulsion polymerization. The effect of various experimental parameters, such as varying the amount of the monomer, initiator, and the emulsifier in the feed on the grafting (%) has been investigated in detail. The maximum grafting (296%) was achieved with 6% (w/v) monomer, 0.15% (w/v) initiator, and 1% (w/v) emulsifier concentration. The nitrile groups of the PAN-grafted silica composite particles were converted into amidoxime by treating with hydroxylamine. The synthesized products in all the preparation steps were carefully characterized by various analytical tools, i.e., Fourier Transform InfraRed (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM), and X-Ray Diffraction (XRD) analysis. In the FT-IR spectrum of the silica-grafted PAN, the appearance of the characteristic peak at 2245 cm^{-1} that corresponds to CN stretching confirms the successful grafting of PAN onto the modified silica particles; while the transformation of nitrile into amidoxime functionality was verified by the appearance of peaks at 1642 cm^{-1} and 920 cm^{-1}. Further verification of the grafting of PAN and amidoxime formation also comes from the SEM micrographs and the XRD profiles. Finally, the obtained amidoxime-grafted silica composite particles were evaluated as an adsorbent for Cu^{+2} ions from the simulated wastewater for potential application in wastewater treatment. The maximum adsorption capacity of 130 mg/g was achieved at pH 5 in 2 hrs.*

KEYWORDS: *Composite; Grafting; Silica; Emulsion polymerization; Amidoxime; Wastewater treatment.*

INTRODUCTION

In recent years a variety of organic-inorganic hybrid composite materials have been synthesized and applied in different fields. These hybrid materials exhibit the combined properties of both the inorganic constituent

as rigidity, high thermal and mechanical stability, and of organic part as surface functionality, i.e., desired functional groups, more flexibility, easy processibility, and etc. These properties make the composites attractive for a wide range of applications, including semiconductors [1], aeronautics, wind-power engineering, and telecom sector [2], automobiles and constructions [3], controlled delivery system [4], and for environmental applications [5]. In environment, composites have found applications in gas sensors for environmental monitoring , photocatalytic systems for the wastewater treatment [6], ion exchange resin [7], and adsorbents for heavy metals and dyes [8, 9]. Alam and coworkers fabricate the organic-inorganic composite materials by incorporation of organic polymers into the inorganic precipitates of multivalent metal acid salts and applied for analytical and environmental applications [10]. These hybrid materials can be obtained by surface functionalization of inorganic oxides such as silica, alumina, end etc. as building blocks of the composites [11, 12]. Among the inorganic oxides, silica has been investigated extensively due to its higher effective surface area, low production cost, and facile surface modification methods [13]. However, due to the presence of hydroxyl groups on the particle surface, it is very difficult to achieve a homogeneous dispersion of the silica particles in a polymer matrix. These hydroxyl groups adhere to each other through hydrogen bonding that leads to agglomeration [14]. To improve dispersion, the surface of the silica particles can be functionalized with various coupling agents; methyltriethoxysilane (MTES), phenyltrimethoxysilane (PTMS), methyltrimethoxysilane (MTMS), and vinyltriethoxysilane (VTES), as a result the silanol groups on the particle surface are replaced with organic moiety, which decrease the aggregation of particles [15, 16].

A wide variety of methods have been employed for the fabrication of silica based composite materials. Among them, the direct mixing of the silica particles and the polymer is the simplest one, that can generally be achieved *via* melt blending [17], solution blending [18, 19] and in situ polymerization [20, 21]. In situ polymerization offers an efficient tool for the preparation of composite materials, where the monomer is directly polymerized on to the modified silica particles [22]. It is a versatile technique for the preparation of composites with controlled morphology. In situ polymerization *via* a heterophase polymerization in aqueous medium has received much attention due to

its environmentally benign experimental conditions. The heterophase polymerization processes are preferred over the bulk polymerizations, due to the easy recovery of the products and lower viscosity of the reaction medium [23]. The solution polymerization also leads to a relatively lower solution viscosity as compared with the bulk polymerization; however, on industrial scale, it is not preferred due to the use of large amounts of the environmentally toxic organic solvents and comparatively slower polymerization rates because of the dilution of the monomers. These problems are avoided in heterophase emulsion polymerization process where the monomers are concentrated in the micelle core and water is used as the dispersion medium [23]. Emulsion polymerization is a common process used in the industry for the production of a number of polymers [24]. A typical emulsion polymerization system has four main components: water (the dispersion medium), monomer, initiator (water soluble), and surfactant (the emulsifier). The water soluble initiator generates the free radicals in the continuous phase where the polymerization process starts [25-27]. However, the propagation step is mainly confined to the micelle core. The termination of the growing chain in the micelle is afforded when another radical enters the micelle core. *Lee et al.* [28] reported the first PMMA-clay hybrid composite synthesized by emulsion polymerization in 1996. Till now, a wide variety of composites have been reported by emulsion polymerization [29, 30].

In the present study, the fabrication and characterization of amidoxime-grafted silica composite particles *via* emulsion graft polymerization has been carried out for potential applications in wastewater treatment. The commercially available silica particles were first functionalized with vinyltriethoxysilane coupling agent that was subsequently employed for the in situ grafting of polyacrylonitrile (PAN) by environment friendly emulsion polymerization process using Tween 80 as the surfactant and potassium persulfate (KPS) as the water soluble initiator. Next, the acrylonitrile groups of the silica-grafted PAN were transformed into amidoxime functionality. Detailed studies have been carried out to investigate the effect of different experimental parameters; monomer, initiator, and surfactant concentration in the feed on the grafting (%). Finally, the obtained amidoxime grafted silica composite particles were evaluated as an adsorbent for Cu^{+2} ions from the simulated wastewater.

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EXPERIMENTAL SECTION
Materials

Isopropanol, vinyltriethoxysilane (VTES), copper sulfate, acrylonitrile (AN), and methanol were purchased from Sigma Aldrich. Dimethyl formamide (DMF) was purchased from Lab-Scan, hydroxylamine from Panreac, Tween 80 from Riedel-de Haen, sodium carbonate from Honeywell and potassium persulphate (KPS) from Merck were used in the present study. All these chemicals were of analytical grade and used as received. Silica was purchased from Amicon Corporation, USA having particle size 35-70 micron, specific surface area 250 m^2/g and pore diameter of 25 nm.

Preparation of amidoxime-grafted silica composite particles
Surface treatment of silica particles

The vinyl functionalization of the silica particles was carried out by a method reported elsewhere [16]. Briefly, silica particles (10 g) were dispersed in water and mechanically stirred for 24 hrs. The resulting suspension was then filtered, washed, and dried in vacuum oven at 50 °C and then grounded. Appropriate amount of silica and isopropanol were taken in glass reactor and mechanically stirred for 30 min, followed by the drop wise addition of vinyltriethoxysilane into the reaction mixture. The temperature of the reaction mixture was raised to 60 °C and the stirring continued for 4 hrs. The reaction mixture was then filtered and washed extensively with methanol and water. The final product was dried in oven and named as Modified Silica (MS) and about 6 % increase in weight was observed.

Emulsion grafting polymerization of acrylonitrile

In a typical experiment, MS (1 g), Tween 80 (1 mL) and water as the dispersion medium with a total volume 100 mL were taken in a three a neck flask fitted with a condenser. The reaction mixture was stirred at room temperature, followed by the addition of acrylonitrile 5 mL and potassium persulfate 0.10 g. After achieving a homogeneous dispersion, the temperature was raised to 70 °C and stirring continued for 6 hrs. The product was filtered and washed extensively with water and acetone. Homopolymer (PAN) and unreacted monomer were removed by soxhlet extraction with DMF for 6 hrs. Soxhlet extracted samples were dried in oven and named

as S-*g*-AN. The Grafting (%) was estimated by using the following equation:

$$Grafting(\%) = \frac{W_f - W_i}{W_i} \times 100 \qquad (1)$$

Where W_f and W_i are the weights of S-*g*-AN and MS, respectively.
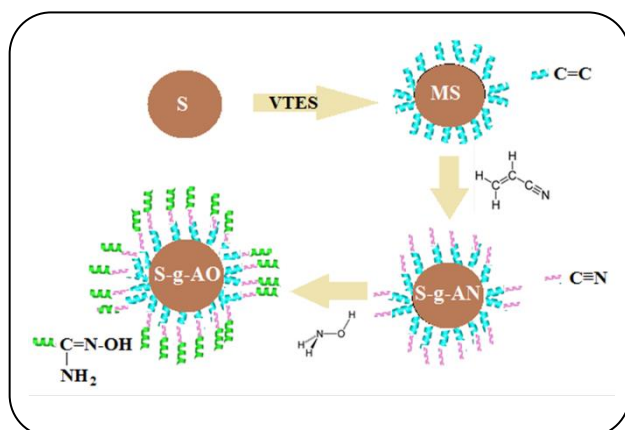
Amidoximation of S-g-AN

The nitrile groups (CN) of the synthesized S-*g*-AN were transformed into amidoxime by treating with hydroxylamine. In a typical experiment, 5 g of S-*g*-AN was taken in a round bottom flask and followed by addition of 100 mL of hydroxylamine solution in (water : methanol, 1:1 v/v). The temperature of reaction mixture was raised to 70 °C and a continuous stirring was carried for 4 h. The resulting product was filtered, washed with 2 % methanol, and dried in vacuum oven at 50 °C. The product was named as S-*g*-AO.

Characterization

Fourier Transform InfraRed (FT-IR) spectroscopy was carried by using Nicolet 6700 FT-IR spectrophotometer from Thermo Electron Corporation, USA, using attenuated reflectance mode. FT-IR spectra at a resolution of 6 cm^{-1} in the range from 4000 to 400 cm^{-1} and 100 scans were recorded for each sample to obtain a high signal to noise ratio. Tescan, MIRA-3 field emission scanning electron microscope was used to investigate the morphology of S-*g*-AN. Sample used in the SEM tests was deposited directly onto the stub and examined without further treatment. The X-Ray Diffraction (XRD) investigations were carried out with Panalytical Xpert Pro X-Ray Diffractometer equipped with Cu Kα (1.5418 Å) radiation source, a Ni filter at a setting of 40 kV/30 mA and a scintillation counter detector. The data was recorded over 5-50° 2θ range.

RESULTS AND DISCUSSIONS

The commercially available silica particles were first modified by treating with vinyltriethoxysilane (VTES) to introduce the polymerizable vinyl functionality on the particles surface. Subsequently, acrylonitrile (AN) was polymerized in situ from the surface of the modified silica (MS) particles under emulsion polymerization conditions using potassium persulfate (KPS) as the initiator and Tween 80 as the emulsifier. The obtained S-*g*-AN

Scheme 1: The schematic presentation of the preparation steps in the fabrication of silica-grafted amidoxime (S-graft-AO).

(silica-*grafted*-acrylonitrile) was converted into S-*g*-AO (silica-*grafted*-amidoxime) by transforming the nitrile functionality of the grafted PAN into amidoxime by treating with hydroxylamine. The whole process is outlined schematically in Scheme 1.

Grafting of acrylonitrile on silica surface by emulsion polymerization

The process follows the free radical polymerization mechanism which comprises of three steps, namely initiation, propagation and termination. In the first step water soluble surfactant KPS decomposes and generate sulphate anion radicals.

$$S_2O_8^- + Heat \rightarrow 2SO_4^{\bullet-}$$

These anion radicals react with vinyl groups of MS and monomer and create active centers. These active centers on reaction with monomer propagate PAN grafted chains and homopolymer chains in the reaction mixture. Termination in emulsion polymerization takes place when radical enters a micelle where a radical is already present. The effect of various experimental parameters; the concentration of monomer, initiator, and surfactant on the grafting has been thoroughly investigated.

Effect of monomer concentration

Grafting (%) was significantly affected by monomer concentration in the reaction mixture. The effect of monomer concentration on grafting (%) was investigated by changing its concentration from 2% (w/v) to 8% (w/v) and the results are depicted in Fig. 1.

These results (Fig. 1) indicate that grafting initially increases with increasing monomer concentration and after reaching a maximum decreases with further increase in monomer concentration. This shows that at lower concentration, the amount of monomer is insufficient as compared to the available active sites for polymerization and when the amount of the available monomer is increased in the reaction mixture more and more monomer molecules are available for reaction with the available active sites and hence the grafting (%) increases. Maximum grafting of 199 % was achieved at 6% (w/v) monomer concentration indicating that 6% (w/v) is the optimum monomer concentration to achieve the maximum grafting. The decreasing grafting (%) with monomer concentration above 6% (w/v) could be attributed to the increased homopolymerization, which decreases the diffusion of monomer and oligomer to the particle surface. Pulat and coworkers reported the similar investigations during chemically induced graft copolymerization of acrylic acid, acrylamide, crotonic acid, and itaconic acid onto cotton fibers [31]. They have reported that the increase in monomer concentration increased the diffusion of the monomer molecules into the fiber structure and as a result high grafting is achieved. The decrease in grafting yield at higher monomer concentrations can be explained by the enhancement of homopolymer formation at that stage.

Effect of initiator concentration

The effect of initiator concentration on grafting (%) was investigated at a fixed monomer concentration 6% (w/v) and the results are depicted in Fig. 2.

It can be seen from the data in Fig. 2 that grafting (%) was significantly lower at 0.05% (w/v) initiator concentration indicating that this concentration is insufficient to generate enough free radicals in the reaction mixture. On increasing the initiator concentration a sharp increase in grafting (%) was observed up to 0.1%. (w/v) above which only a slight increase in grafting (%) could be observed. The enhancement in grafting (%) with initiator concentration indicates that the free radicals generated by the dissociation of the KPS take part in the polymerization process. A maximum grafting of 296 (%) was achieved at 0.15% (w/v) indicating that 0.15% (w/v) initiator concentration is sufficient with 6% (w/v) monomer concentration to produce the maximum grafting (%).
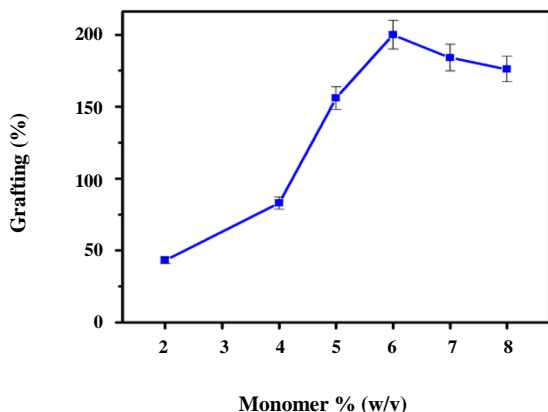
Fig. 1: Effect of monomer concentration on grafting (%) at 0.1% (w/v) initiator and 1% (w/v) surfactant concentration.
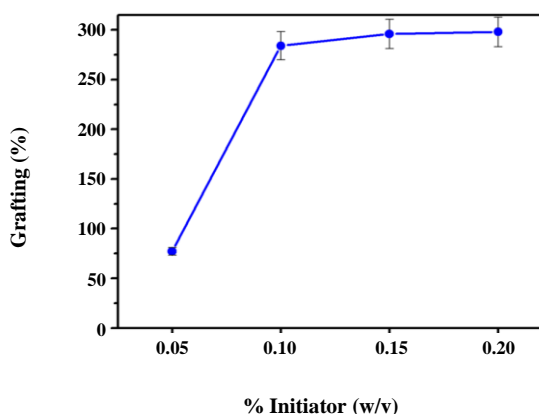

Fig. 2: Effect of initiator concentration on grafting (%) at 6% (w/v) monomer and 1% (w/v) surfactant concentration.
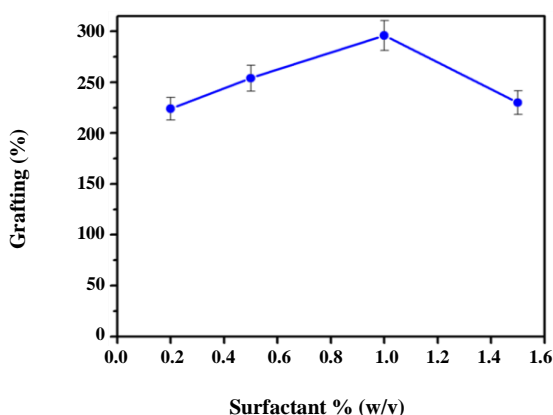

Fig. 3: Effect of the surfactant concentration on the grafting (%) of polyacrylonitrile at 6% (w/v) monomer and 0.15% (w/v) initiator concentration.

On further increase in KPS concentration beyond 0.15% (w/v) the extra free radicals remain in the reaction medium and hence no more increase in grafting was observed. Similar trend has also been reported by *Zare* and *coworkers* [32], where they have studied the effect of monomer types and concentrations, temperature, and initiator concentrations on the grafting copolymerization of poly(lactic acid) (PLA) with amide monomers using benzoyl peroxide as the initiator.

Effect of surfactant concentration

Surfactants are used in emulsion polymerization processes, pharmaceutical, and cosmetic products. In emulsion polymerization, surfactant play important role during nucleation and growth stages and also affects the particle size, size distribution, rate of polymerization, polymer molecular weight, and particle morphology [24]. The chemical structure and amount of the surfactant used have a strong influence on viscosity and stability of the latex [24]. In the present study Tween 80 was used as surfactant due to its low toxicity and cost. It is used in food, health, and beauty products, medicine, and etc. The effect of surfactant concentration was investigated by keeping the monomer and initiator concentration constant; (6% (w/v) and (0.15% (w/v), respectively, and varying the surfactant concentration in the range from 0.2 to 1.5% (w/v) and the results are depicted in Fig. 3.

The results reveal an initial increase in grafting (%) with increase in surfactant concentration up to 1% (w/v) and then decreases with further increase in surfactant concentration. The decrease in grafting (%) beyond 1% (w/v) of surfactant concentration in the reaction medium could be due to greater micelle population and that both the initiator and monomer concentration act as limiting factor under these conditions and as a result the grafting (%) decreases. Taimur and his coworkers have made similar observation for the graft polymerization of acrylonitrile onto the sepiolite (clay) [33]. Thus, 1.0% (w/v) surfactant concentration was determined to be the optimum surfactant concentration with 6% (w/v) and 0.15% (w/v) monomer and initiator concentration, respectively, to achieve the best grafting (%) results.

Structural characterization

The FT-IR spectra of the as received silica (unmodified) 'S' and its different modified forms are shown in Fig. 4. The FT-IR spectrum of silica shows
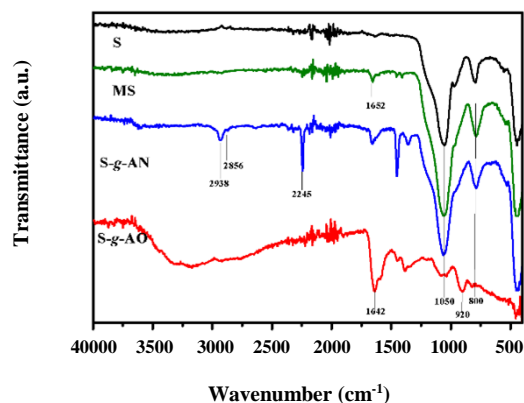
Fig. 4: FTIR spectrum of unmodified silica (S), modified silica (MS), acrylonitrile-grafted silica (S-g-AN) and amidoxime-grafted silica (S-g-AO).

absorption bands at 1050, 960 and 800 cm^{-1} arising from the asymmetric vibration of Si–O, asymmetric vibration of Si–OH, and symmetric vibration of Si–O, respectively [34]. The spectrum of MS reveals a new peak at 1652 cm^{-1} arising from vinyl groups (C=C) of the attached VETS. The presence of vinyl groups indicates that the silica was successfully functionalized with VTES. Moreover, the increase in intensity of the peaks arising from siloxane groups is due to additional Si–O–C linkages due to modification [35].

The grafting of PAN on the surface of the MS could also be validated by FT-IR spectroscopy. The appearance of new sharp peak at 2245 cm^{-1} attributed to the C≡N stretching of PAN suggests the successful grafting of PAN to MS [36]. Moreover, new signals appeared at 2856 cm^{-1}, 2938 cm^{-1}, and 1455 cm^{-1} corresponding to the asymmetric and symmetric stretching and bending deformation of –CH$_2$ groups of the PAN backbone could also been in the spectrum [37]. The conversion of nitrile groups into amidoxime functionality was verified by the disappearance of peak at 2245 cm^{-1} and appearance of new peaks at 1642 cm^{-1} and 920 cm^{-1} arising from C=N and N–O stretching. In addition, the FTIR spectrum of S-*g*-AO also shows a broad band at 3000-3500 cm^{-1}, which was assigned to NH and OH of amidoxime functional groups [38].

Morphology of the silica particles before and after grafting was analyzed by SEM and the results are depicted in Fig. 5. The unmodified silica particles 'S' have irregular morphology and smooth surface (Fig. 5), while after

grafting with PAN, the surface becomes rougher and scraggy that could be due to spotty grafting of PAN on the surface. Further confirmation of the successful grafting of PAN to silica surface comes from the EDX spectra shown in Fig. 5. The EDX spectrum of 'S' indicates the presence of **Si** and **O**, while the spectrum of S-*g*-AN reveals the signal of nitrogen (**N**) along with **Si** and **O**. The presence of **N** in the EDX spectrum of S-*g*-AN clearly confirms the grafting of PAN on silica surface.

The XRD diffractograms of S, MS, S-*g*-AN, and S-*g*-AO are shown in Fig. 6. For 'S' a broad halo centered at approximately 2Θ = 22 ° indicating the amorphous nature of silica can be seen in Fig. 6. The broad halo retains its position even after functionalization with VETS, grafting of PAN, and amidoximation, which indicates that silica conserves its structural integrity during these reactions. The XRD pattern of S-*g*-AN reveals a crystalline peak at 2Θ = 17 ° that arises from (100) reflection of grafted PAN chains in addition to the amorphous halo at 22 ° [39-41]. The disappearance of the crystalline peak at 17° in S-*g*-AO further verifies that the grafted PAN chains were successfully transformed into polyamidoxime chains.

The prepared amidoxime grafted silica as adsorbent for copper ions

For potential application in wastewater treatment, the obtained S-*g*-AO was investigated as adsorbent for copper ions from simulated wastewater and the results of the calculated adsorption capacities (mg of the copper/g of the S-*g*-AO) after 2 hrs contact time as a function of pH are plotted in Fig. 7.

The data show that the adsorption capacity increases with increasing pH of the medium and reaches a maximum value of 130 mg/g for S-*g*-AO and bare silica shows a maximum adsorption capacity of 20 mg/g at pH 5. No adsorption was observed at pH > 5 that was attributed to the precipitation of copper. The effect can be explained on the basis of interaction mechanism of amidoxime group with metals as reported in our previous study [16]. The amidoxime group exhibits amphiprotic character and at lower pH the basic amino group of amidoximes will be highly protonated and displaying cationic character. While at higher pH, the acidic hydroxyl group of oxime will dissociate, and exhibiting anionic character. At lower pH, the amino groups of amidoximes will lose their complexation ability towards metal ions leading to lower adsorption capacity at acidic pH. On the other hand, as the pH
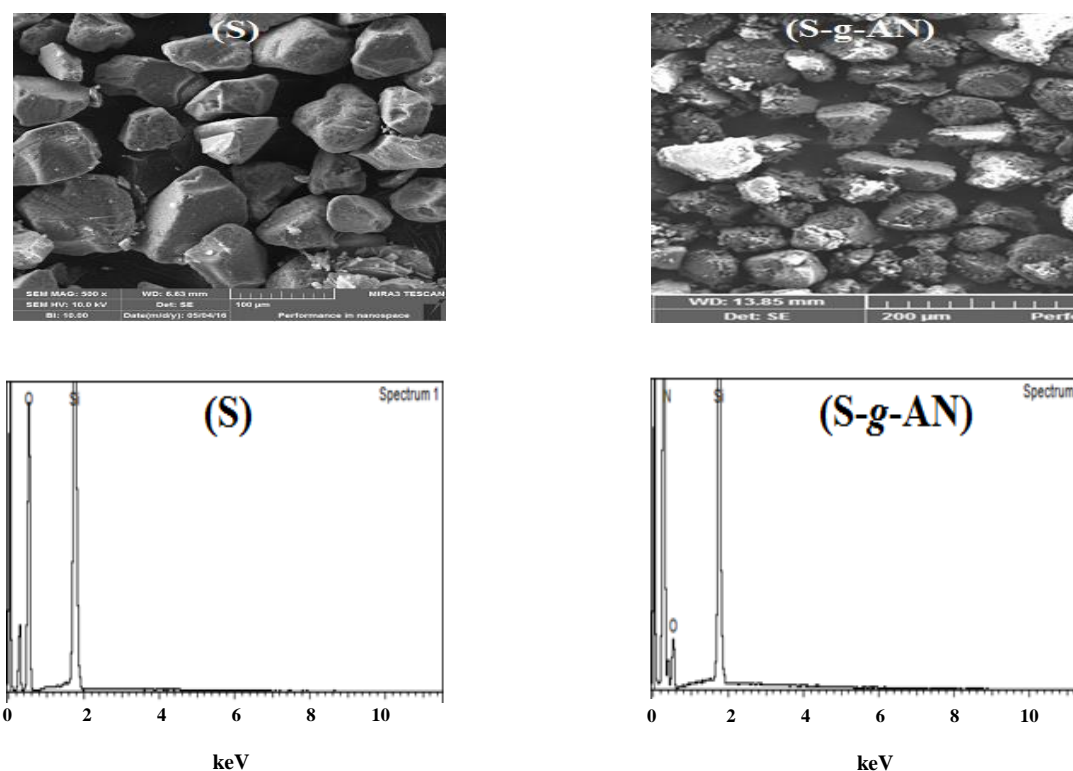
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Fig. 5: SEM micrographs and the respective EDX spectra of unmodified silica (S), silica-grafted-acrylonitrile (S-g-AN).
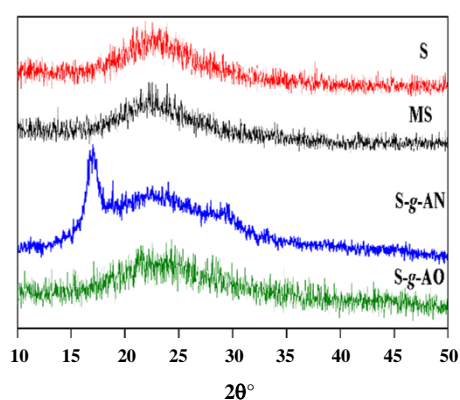

Fig. 6: X-ray diffraction patterns of S, MS, S-g-AN and S-g-AO.

Fig. 7: Effect of pH on adsorption capacity of Silica and S-g-AO (with grafting 296 %) for Cu2+ ion from simulated wastewater.

increases, the degree of protonation decreases and as a result the coordination and chelating ability of the AO enhances.

CONCLUSIONS

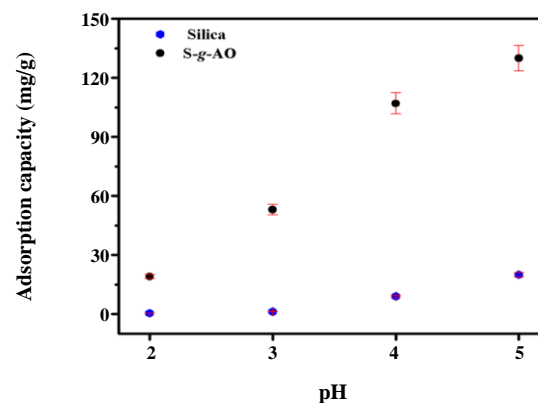Polyacrylonitrile grafted silica composite was synthesized *via* emulsion grafting polymerization and the nitrile groups of the grafted PAN chains were subsequently successful transformed into amidoxime groups by reacting with hydroxylamine. Acrylonitrile was grafted onto silanized silica in aqueous media using tween 80 as surfactant and potassium persulphate as initiator and get a high grafting of 296 % at optimized concentrations

of monomer, initiator and surfactant. This technique proved to be efficient and give high grafting at low monomer concentration. The introduction of vinyl groups, grafting on acrylonitrile and conversion into amidoxime were confirmed by FT-IR spectroscopy. SEM micrographs and XRD analysis also support these results. Moreover this study suggests that the synthesis root is free from the requirements as use of high concentrations of monomer, costly organic solvents or special equipment. Amidoxime grafted silica composite was tested as an adsorbent for Cu^{+2} from simulated waste water and a maximum adsorption capacity of 130 mg/g was achieved at 2 hours.

Acknowledgments

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