

Regenerating of consuming ion-exchange resin by graft polymerization for steam boiler wastewater treatment

Hadi S. Al-Lami*, Mahmood A. Al-Marzok

Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq, Tel. +964 770 737 7488;
email: hadisalman54@yahoo.com (H.S. Al-Lami), Tel. +964 770 313 8150; email: mah_almarzok@yahoo.com (M.A. Al-Marzok)

Received 18 August 2020; Accepted 4 February 2021

ABSTRACT

The cationic sulfonated polystyrene resin is consumed in the production process of water desalting to produce deionized water used to generate steam boilers in different industries. Our target is to reactivate the consumed cationic resin by the grafting process of o-aminobenzoic acid, p-aminobenzoic acid, and acrylamide monomer. The grafting process causes an increasing efficiency of the grafted consumed resin from 54.34% to 55.37%, 56.20%, and 63.22% respectively in removing the boiler's wastewater hardness. The result of grafted consumed resin with acrylamide is engorging to increase the chain length of acrylamide monomer grafted on the resin by free-radical polymerization using benzoyl peroxide initiator in a dry N₂ atmosphere. It increases the efficiency of the consumed resin grafted with polyacrylamide to 83.68%. The same sequence is correct for removing hydrazine used in steam boilers, for metal protection, with efficiency, reaches 100%. Fourier transform infrared spectroscopy confirms evidence of successful grafting processes.

Keywords: Sulfonated polystyrene; Hardness; Grafting; Acrylamide; Hydrazine

1. Introduction

Water is used directly or indirectly in various industries, so the specifications of water used in the industry vary from one to another depending on the type of industry and the role of water in it. Each industry has its water quality considerations. Some industries use raw water directly without treatment and in others, wastewater must be like that of distilled water, so it is not possible to set up general specifications for water used in the industry [1]. Raw water entering an industrial plant often needs treatment to meet tight quality specifications to be of use in specific industrial processes. Industrial water treatment includes all these aspects of boiler water treatment and cooling water treatment. The identification of the range and the possibility of water quality parameters of certain water bodies like rivers

and lakes can give useful guides to prepare for and deal with the consequences of water quality problems [2].

Due to their need for large quantities of water, accurate water quality specifications for many industries are under demand. Most factories have created and developed several techniques to get their water economically by adopting different treatment systems at their discretion, including physical and/or chemical and sometimes vital purification processes depending on the specifications of the water required, and on the quality of impurities in raw water source [3]. Using untreated or improperly treated water can cause disasters such as boiler explosions, damage, and fast corrosion of equipment, and increase the cost of operation and maintenance [4].

The increase in the population and the industrial expansion that the world witnessed in recent decades, has led

* Corresponding author.

to increasing demands for water. The emergence of water shortage problems in some regions of the world, and a rise of river water salinity in some places because of climate change, have also placed a significant impact on the water quality of rivers of the world [5–7]. Therefore, it has become necessary to use water economically because it is one of the main pillars of human and industrial growth. Besides, it exacerbates the problem of environmental pollution. Global attention and pressures on the industry by environmental protection organizations to the industry contribute to the solution of this problem. The modern industrial project's plan not only aims at building industrial wastewater processing units but also establishing internal networks and developing studies to dispose of waste hunted by these units [3,8].

For industrial companies using boilers for their facility, some types of boilers feed water treatment system is usually necessary to make sure an efficient process and quality steam generation. The most important pollutants in industrial water draining from boilers are thermal pollution affecting the aquatic environment, salt concentration, and acid function. It increases the range of dissolved salts that represent the total salinity resulting from the presence of various salts. Desalination units in reverse exudation apply saltwater extracted from desalinated water to the river through the concentrated saltwater drainage pipe, and Ansari et al. [9] explained that introducing industrial minerals-containing salts leads to the eutrophication phenomenon. Besides, it also increases water pollution by releasing hydrazine used in water treatment for corrosion protection purposes in the river.

The study issued by the World Health Organization (WHO) has shown that hydrazine with limited concentrations affects the nervous system, the liver, and kidneys of humans [10]. They found that the concentration of hydrazine that is lethal for half the number of fish in a population (LC50) exposed for 1–4 d, ranged from 0.54 to 5.98 mg/L [11]. Therefore, the overall water quality is sometimes difficult to test because of large sample sizes and extensive analytical suited parameters [12,13]. Although some monitored parameters could be analyzed either alone or grouped according to a common feature, such analysis provides partial information on the overall quality [14].

Considering the various industrial uses of large quantities of ion exchange resins where they were consumed after being used for specified periods, depending on the operating conditions, they ought to be replaced by new ones leaving tons and tons of these consumed to be thrown away. Therefore, this study is engaged in recycling, reactivation, and increasing the efficiency of cationic sulfonated polystyrene resin consumed in the production of deionized water for steam boilers in an electrical power station. The resin reactivation was carried out by grafting of *o*-aminobenzoic acid (OABA), *p*-aminobenzoic acid (PABA), and acrylamide monomer (AAM) and extending the chain length of the latter by free-radical grafting polymerization to prepare four different new resin derivatives and namely; *o*-aminobenzoic acid-grafted-resin (OABA-g-resin), *p*-aminobenzoic acid-grafted-resin (PABA-g-resin), acrylamide-grafted-resin (AAM-g-resin), and polyacrylamide-grafted-resin (PAAM-g-resin) respectively. We will use the reactivated ion-exchange resins for water desalination to remove metals

causing water hardness, especially calcium and magnesium, and hydrazine from steam boilers water drainage as it is highly toxic.

2. Experimental

The present study was conducted in the Department of Chemistry/College of the Science/University of Basrah in collaboration with the Hartha Power Station, General Directorate of Energy Production in Basrah/Iraq. They provided us with the consumed strong cationic sulfonated polystyrene resin and all boiler wastewater samples used in this work.

2.1. Materials and measurements

Consumed strong cationic sulfonated polystyrene resin having the proposed chemical structure shown in Fig. 1, type Purolite type was supplied by Hartha Power Station (Basrah/Iraq) which was available in the stores and yards in large quantities with properties listed in Table 1 [15]. *o*-aminobenzoic acid (OABA), *p*-aminobenzoic acid (PABA), and acrylamide monomer (AAM) with a purity of 99% were purchased from Merck (UK). Benzoyl peroxide (Bz₂O₂) was used as an initiator. Toluene and ethanol solvents were purchased from Sigma-Aldrich Company (Germany).

All other reagents (analytical grade) were used as received. We used deionized water for preparing all solutions and for rinsing the resins in all experiments.

Fourier transform infrared spectroscopy (FTIR) was used to show the functional groups of the consumed resin and the added functional groups of the OABA, PABA, AAM, and PAAM grafted derivatives to be evidence of the grafting reaction, and this was done on the Shimadzu 8101M spectrophotometer (Japan) using potassium bromide discs between (4,000–400 cm⁻¹) under resolution 4 cm⁻¹.

2.2. Resin preparation for grafting process

The operational processes of water treatment units affect resins of various kinds in terms of granular condition, where a percentage of broken granules and the granules consumed because of the contaminants; therefore, they require some work to prepare the consumed resins for grafting by the following processes.

2.2.1. Physical processes

This process was used to remove the broken granules with diameters of less than 0.3 mm by wet sieving to eliminate fragments and broken beads and separate them from perfect beads. Fig. 2 shows the resin granules before and after the sieving process.

2.2.2. Chemical treatment

Iron salts, especially oxidized from ferrous to ferric ions were removed by washing the resin with distilled water and soaking it with 10% hydrochloric acids for 24 h. This will also remove calcium and magnesium ions deposit on the surface and around resin granules.

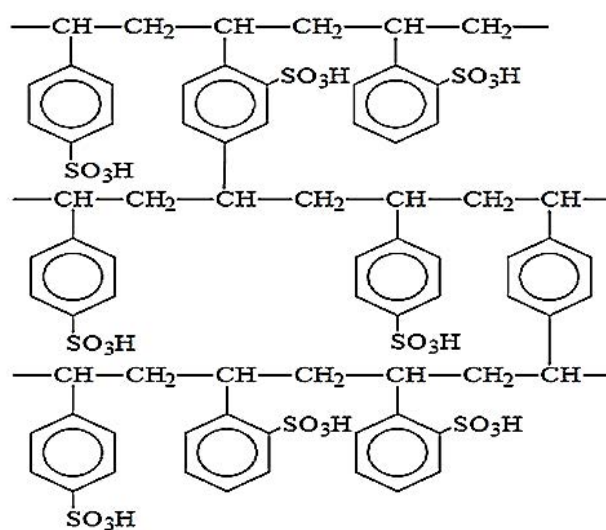


Fig. 1. Chemical structure of the sulfonated polystyrene resin.

Table 1
Physical properties of the consumed resins used [17]

Trade name	Purolite C-100
Color	Dark brown
Shape	Heterogeneous granules
Solubility	Not soluble
Fusion	Not melting
Particle size	0.3 mm < 1% 1.2 mm < 5%
Specific gravity	1.29
pH limit	0–14

Organic materials contaminating the resin were removed by soaking the resin with a 20% sodium chloride solution or by using 10% sodium hydroxide solution for 24 h in both cases.

2.3. Preparation of acrylamide, *o*-aminobenzoic acid, and *p*-aminobenzoic acid-grafted-resin

The grafting of consumed resin with different functional organic molecules was carried by weighing 50 g from washing resin and placing them in a 250 mL 2-neck round bottom flask filled with 150 mL distilled water and equipped with a magnetic stirrer, and then 5 g of acrylamide (AAM) monomer was added. The mixture was left stirring for 3 h at 40°C to complete the grafting process. Afterward, the resin was washed several times with distilled water to remove the un-grafted monomer that might be present [16,17].

The same procedure was repeated to graft *o*-aminobenzoic acid (OABA) and *p*-aminobenzoic acid (PABA) using an ethanol solvent. The grafted and un-grafted resins were checked by FTIR.

Percentage grafting G (%) was gravimetrically determined as percentage weight using Eq. (1) [18,19]:

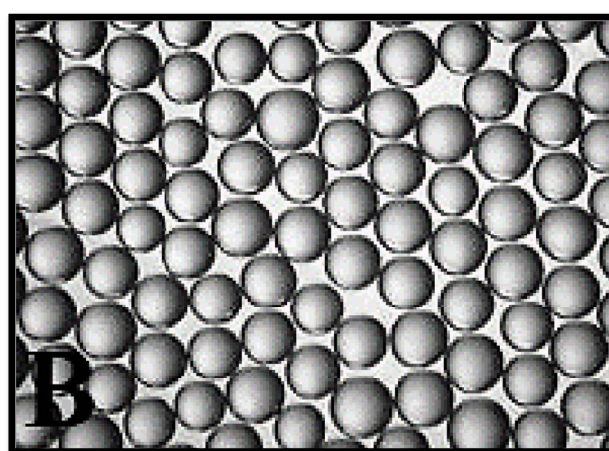
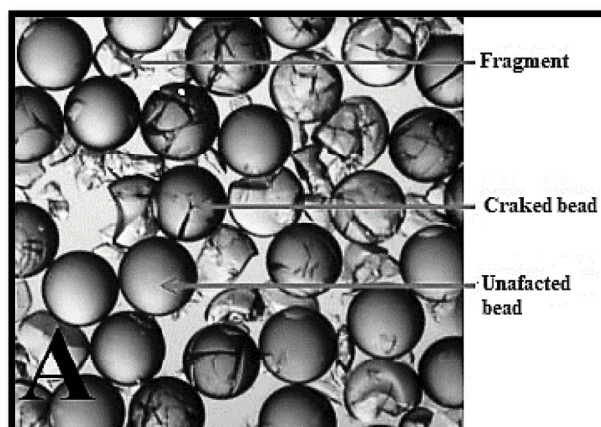


Fig. 2. Consumed resin granules (a) before and (b) after the sieving process under an optical microscope.

$$G(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 is the weight of the resin before grafting process and W_2 represent the weight of grafted resin after washing and drying. The percentage of grafted resin by PABA, OABA were 68% and 73% respectively.

2.4. Preparation of polyacrylamide-grafted-resin

The free radical graft polymerization reaction of the acrylamide monomer was carried out to extend the acrylamide-grafted-resin chain in the 3-neck round bottom flask equipped with a thermometer and magnetic stirrer and dry N₂ gas inlet. 10 g of the acrylamide-grafted-resin was added to the 20 mL of dry toluene. The free-radical grafting polymerization was proceeding under dry N₂ gas in a water bath after adding benzoyl peroxide (1×10^{-3} mol/L) at 70°C [17,20,21]. The product was poured into water to remove the unreacted acrylamide monomer and polyacrylamide homopolymer might be formed. The polyacrylamide-grafted-resin was filtered and washed several times with water and with acetone, then it was vacuum dried at 50°C. The percentage of grafted polyacrylamide resin was 75%.

2.5. Determination of total hardness of boiler wastewater

Total water hardness is commonly determined by the titration of a water sample with a standardized solution of ethylenediaminetetraacetic acid (EDTA) using Eriochrome Black T as an indicator [22]. This procedure was carried out by taking a water sample volume of 25 mL (V mL), then 1 mL of ammonia buffer was added to bring the pH to 10 ± 0.1 , followed by the addition of 1 or 2 drops of the Eriochrome Black T indicator solution. The solution turned wine red indicating calcium or magnesium hardness. The mixture was titrated against EDTA with vigorous shaking till the wine red color just turned blue implying that the endpoint was reached. Total hardness can be calculated using Eq. (2) [22,23]:

$$\text{Total hardness (mg/L)} = \frac{V_1 \times N \times 100 \times 1,000}{V} \quad (2)$$

where V (mL) is the volume of the water sample taken and V_1 (mL) is the volume of EDTA with N normality. All samples were assessed in triplicate and results were reported as a mean value.

2.6. Determination of hydrazine in industrial water

The determination of hydrazine usually made on boiler wastewater, and other waters treated with hydrazine (N_2H_4) to give protection where reducing conditions are required, particularly in mixed metallurgy systems for protecting copper alloys. This reducing chemical reacts with dissolved oxygen to form nitrogen and water [24]. The chemical reaction with oxygen can be expressed in the following equation:



Hydrazine in polluted boiler wastewater was determined by mixing 50 mL of the water sample with 8 mL of 3% hydrochloric acid. Then, 10 mL of p-dimethylaminobenzaldehyde was added to the mixture and left to stand for 10 min. The resulting colored condensation product was determined spectrophotometry using its maximum absorption at $\lambda = 450$ nm [22,25]. All samples were evaluated in triplicate and results were reported as a mean reading.

3. Results and discussion

3.1. FTIR examination of the consumed resin

The FTIR spectrum of the consumed strong positive ion exchange resin showed many distinctive peaks at certain frequencies, Fig. 3. The broadband appeared at 3,285–3,458 cm^{-1} characteristic of the vibration of the O–H group of ($-SO_3H$). The FTIR spectrum also showed a strong distinguishing peak at 1,414 cm^{-1} associated with the (S=O) stretching of the sulfonyl group [26], a weak band at 3,018 cm^{-1} due to aromatic (C–H) and at 2,856 cm^{-1} assigned for (C–H) aliphatic. It also showed a peak at 1,639 cm^{-1} attributed to the aromatic (C=C) bond [27].

3.2. FTIR examination of the grafted consumed resin with PABA and OABA

The FTIR spectra recorded for the grafted consumed resin with PABA and OABA are shown in Figs. 4 and 5 respectively. The spectrum of PABA-grafted-resin shows a strong band at 1,167 cm^{-1} that belong to the sulfonamides (SO_2-NH) group [28,29], and it appeared between the two original large and intense two bands at 1,242–1,121 cm^{-1} which are attributed to both the resin aromatic C–H and S=O groups, respectively [26]. A peak is also shown in 3,485–3,450 cm^{-1} assigned to the –OH group of the resin sulfonyl group ($-SO_3H$), as well as a sharp stretching peak of the aromatic (C=C) bond at 1,614 cm^{-1} . The grafting process

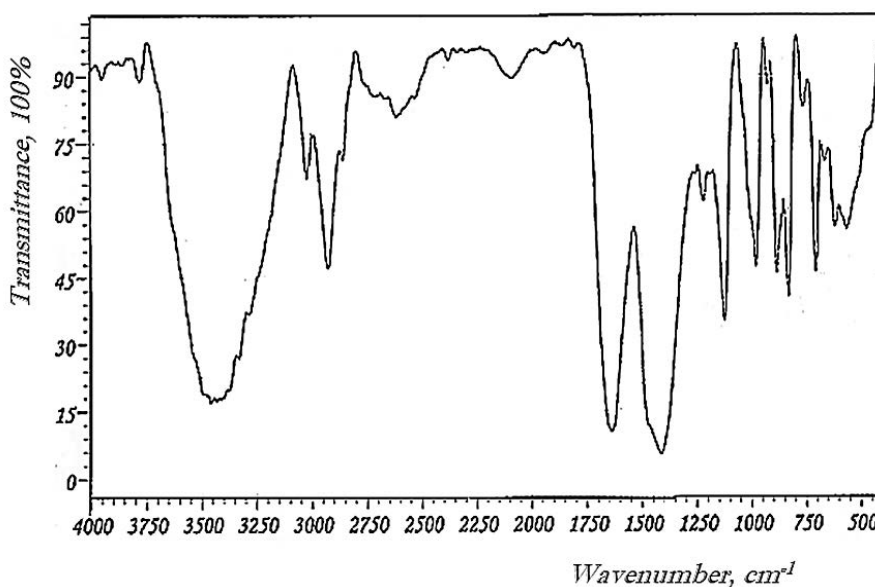


Fig. 3. Infrared spectrum of washed consumed strong positive resin.

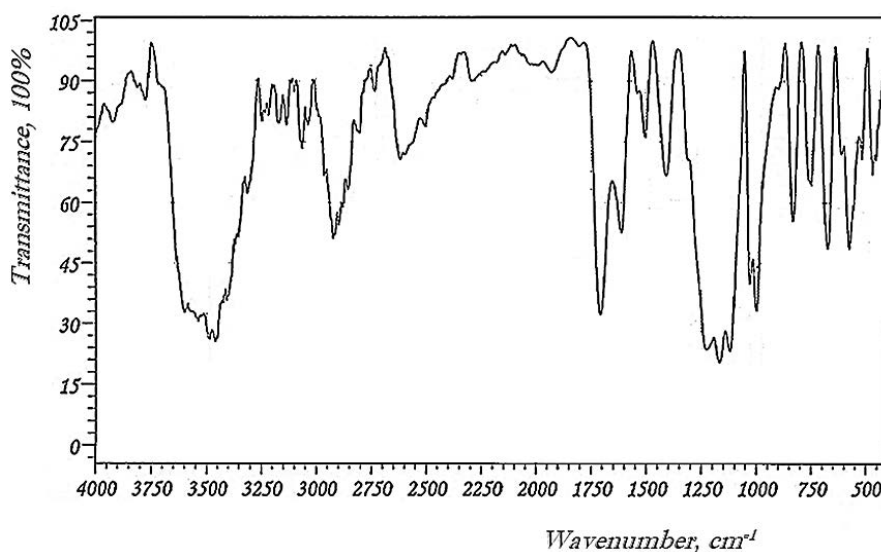


Fig. 4. Infrared spectrum of consuming resin grafted with PABA.

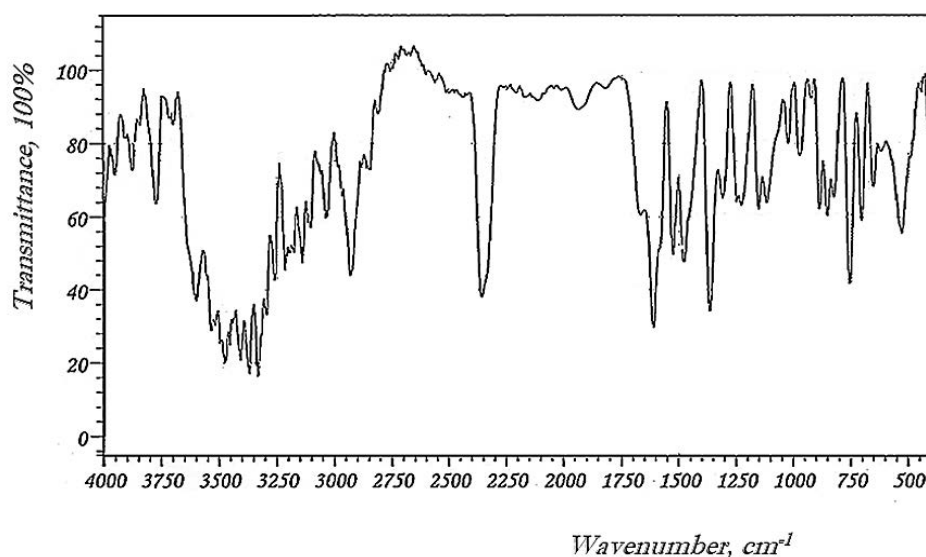


Fig. 5. Infrared spectrum of consuming resin grafted with OABA.

is confirmed by the appearance of an intense peak associated with stretching vibration of carbonyl amide (C=O) group at $1,708\text{ cm}^{-1}$, accompanied by a strong band at $3,400\text{--}3,330\text{ cm}^{-1}$ assigned for the (N–H) group confirming the formation of acid structure-grafted-resin [26,27], and it can be represented by the chemical equation shown in Fig. 6.

The infrared spectrum of the consumed resin grafted with p-aminobenzoic acid monomer shown in Fig. 4, does not differ that much from the spectrum obtained with o-aminobenzoic acid monomer grafted consumed resin, Fig. 5, except for the appearance of new broadband between $(3,599\text{--}3,103)\text{ cm}^{-1}$. This implies the formation of a hydrogen bond between the o-aminobenzoic acid carbonyl group and the resin sulfonamides group [27,28], and this can be represented by the equation shown in Fig. 7.

A band can also be observed at $1,153\text{ cm}^{-1}$ assigned for the symmetric stretching vibration of the (S=O) sulfonamides ($\text{SO}_2\text{-NH}$) group where it was not of the expected strength due to the formation of the hydrogen bond. Consequently, it has caused a hampering to the grafting process of the OABA in contrast to the grafting of the PABA monomer. The strong peak at $1,612\text{ cm}^{-1}$ is due to the stretching of the aromatic (C=C) group, and the appearance of the carbonyl group (C=O) at $1,666\text{ cm}^{-1}$, which was not by the usual intensity for the same reason of the formation of the hydrogen bond [27]. In addition to that, the usual stretching peak at $3,040\text{ cm}^{-1}$ is attributed to (C–H) aromatic group, and that of the aliphatic group appeared at $2,932$ and $2,844\text{ cm}^{-1}$ symmetric and asymmetric stretching vibration respectively [26,27].

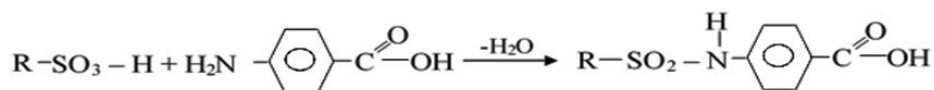


Fig. 6. Chemical equation of grafting PABA onto consuming resin.

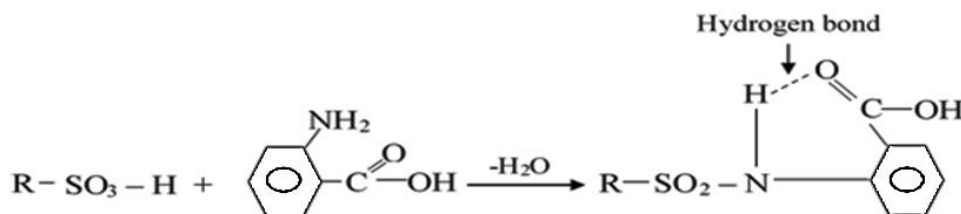


Fig. 7. Chemical equation of grafting PABA onto consuming resin.

3.3. FTIR examination of the grafted consumed resin with AAM and PAAM

Acrylamide was also used to graft the consuming positive resin, which is a vinyl type monomer with the amide pendant group. The FTIR spectrum of the resin-grafted-acrylamide monomer appeared as expected; the characteristic absorption band at 3,496–3,234 cm^{-1} attributed to the -NH group conforming with the -OH of the sulfonyle $\text{-SO}_3\text{H}$ group [26], Fig. 8. Besides the characteristic absorption peak at 1,178 cm^{-1} assigned to the stretching vibration of the S-N of the sulfonamides $\text{SO}_2\text{-NH}$ group confirming the formation of resin-AAM structure, and Fig. 9 illustrates the representative chemical equation of the grafting process.

The FTIR spectrum of resin-grafted-AAM, Fig. 8 shows a strong band at 1637 cm^{-1} corresponded to stretching vibration of the amide carbonyl (NH-C=O) group [28,29]. It is overlapped with the aliphatic and aromatic (C=C) bonds as they are supposed to appear at about 1,620 and become wider than in the case of grafting PABA and OABA shown in Figs. 4 and 5 respectively, implying the correctness of

the grafting process of AAM monomer onto the consuming resin [28]. The evidence of the presence of the aliphatic (C=C) monomers double bond comes from the presence of two strong peaks at 1,080 and 1,042 cm^{-1} assigned to the (C-H) out of plane deformation associated with (C=C) double bond [28,29]. Also, the presence of a peak at 3,069 cm^{-1} attributed to the aliphatic (C-H) attached to the (C=C) in the (-C=CH_2) group besides that of the aliphatic group that appeared at 2,922 and 2,854 cm^{-1} assigned for symmetric and asymmetric (C-H) stretching vibration respectively [27].

The grafted AAM monomer on the resin was extended by grafting the free-radical polymerization of the additional AAM monomer in the presence of the benzoyl peroxide initiator as described in (section 2.4). The infrared spectrum of the polyacrylamide-grafted-resin is shown in Fig. 10. Mostly, it shows the same peaks as in the FTIR spectrum of the AAM-grafted-resin (Fig. 8).

The most important peak observed at 1,666 cm^{-1} is assigned for stretching vibration of the carbonyl amide group (-CO-NH), and it appears in a higher wavenumber than where it has appeared at 1,637 cm^{-1} in the case of

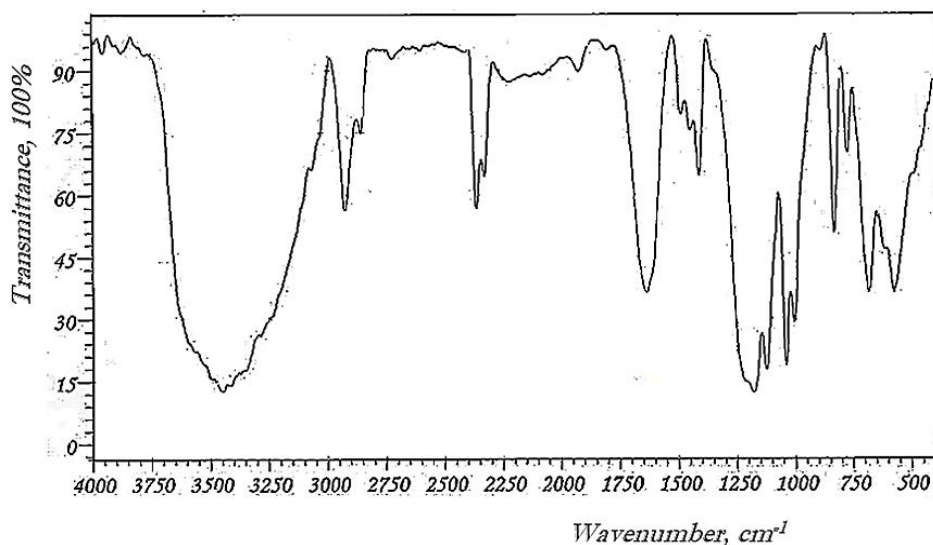


Fig. 8. Infrared spectrum of consuming resin grafted with AAM.

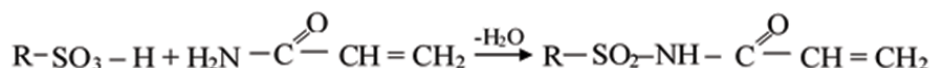


Fig. 9. Chemical equation of grafting AAM onto consuming resin.

Table 2

Important functional groups and their assignment, present in the resin-grafted-PAAM infrared spectrum

Functional	Bond	Stretching vibration (cm^{-1})
SO_2NH	S–N	1,178
NHCO	C=O	1,666
Aromatic	C–H	3,030
Aliphatic	C–H	2,924 + 2,856
Sulfonamide	$\text{SO}_2\text{N-H}$	3,309–3,483

grafting of AAM monomer onto the resin, Fig. 8. This is attributed to the disappearance of the ($-\text{C}=\text{C}-$) double bond of AAM which confirms the polymerization of acrylamide monomer [30,31], and this can be shown schematically in Fig. 11. The most important infrared spectrum assignment of the polyacrylamide-grafted-resin is listed in Table 2.

3.4. Estimation of the grafted consumed resin efficiency

This research was carried out on the use of grafted consumed resin derivatives for the removal of total hardness caused by calcium and magnesium metal ions and hydrazine from wastewater that comes out from the boilers of the Hartha Power Station.

3.4.1. Total hardness

Hardness may be present in water ranging from zero to several hundred mg/L. The calculation of hardness in

water by EDTA titration is used since it can be found by adding a small amount of Eriochrome Black T indicator to the aqueous solution containing Ca^{++} and Mg^{++} ions at a pH of 10 ± 0.1 forming wine red (Ca-EBT and Mg-EBT) complex [22,23]. EDTA has a stronger affinity towards Ca^{++} and Mg^{++} . Hence, if EDTA is added, the former complex (Ca-EBT and Mg-EBT) is broken and new complexes (Ca-EDTA and Mg-EDTA) of blue color are formed. When all the ions are complexed, the solution is turned blue, which indicates the endpoint of the titration. This method is applied using the consumed resin and its grafted derivatives.

Table 3 shows the comparative percentage efficiency of total hardness removed from water samples using the consumed resin directly and the resin grafted with OABA, PABA, AAM, and PAAM. As expected, the efficiency of the consuming resin to remove water hardness is low, which is 54.34%. Grafting resin with OABA and PABA did not make that much difference from the efficiency point of view and was 55.37 and 56.2 respectively. It seems that the presence of the acidic carboxyl groups didn't show the expected activity toward metals causing water hardness, and the main idea was to carry out the grafting process and then increase the chain through condensation polymerization by adding more measure of the amino acid monomers which do not happen in this case.

It ought to say here that the re-efficacy of the consumed resin by grafting OABA and PABA is not encouraging in terms of withdrawing hardness ions despite the success of their association with the resin. So, it was thought of another monomer from another type of vinyl amine monomer, and the acrylamide priority comes first, where the amine group can be used for grafting on the resin and

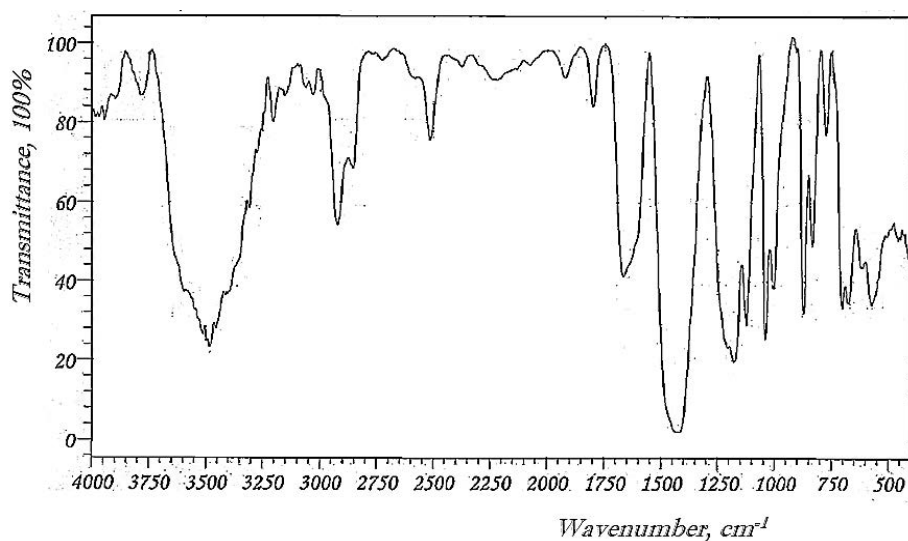


Fig. 10. Infrared spectrum of consuming resin grafted with PAAM.

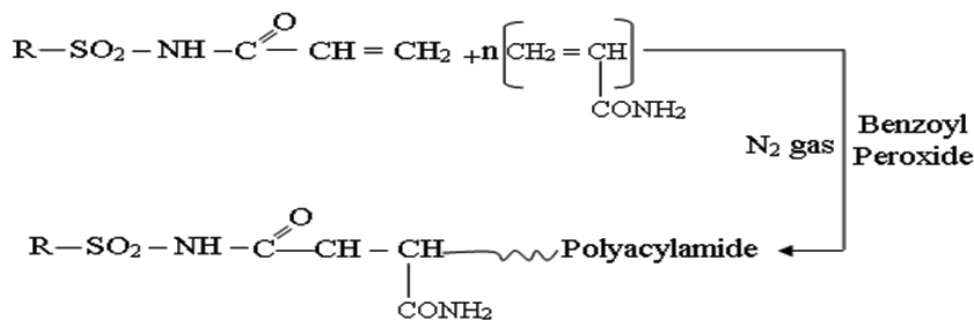


Fig. 11. Chemical equation of extending grafted AAM to PAAM onto consuming resin.

Table 3

Efficiency of the consuming resin and its grafted derivatives with various monomers and polyacrylamide toward water hardness

Resin	Concentration of boiler wastewater hardness before treatment (mg/L)	Concentration of boiler wastewater hardness after treatment (mg/L)	Efficiency (%)
Un-grafted resin	4.84	2.21	54.34
Resin-g-OABA	4.84	2.16	55.37
Resin-g-PABA	4.84	2.12	56.20
Resin-g-AAM	4.84	1.78	63.22
Resin-g-PAAM	4.84	0.79	83.68

the vinyl ($-C=C$) can be used in polymerization when the presence of extended polymer chains is needed to function the reactivated resin by grafting process. The same conclusion was made by Sultan et al. [17] on the functionalization of alumina ceramic powders by acrylic acid monomer and extended it to poly(acrylic acid) polymer for removing phenol and phenol derivatives from industrial wastewater, and Singh et al. [31] on functionalizing chitosan as an efficient adsorbent for removing azo dyes from aqueous solutions.

The reactivation of the consumed resin by grafting of acrylamide monomer has improved its effectiveness somewhat and the efficiency has increased to 63.22% which is considered a good move. To increase this efficiency, one needed to optimize the grafting conditions, therefore, free-radical grafting polymerization was conducted to extend the AAM chain length by polymerizing an extra AAM monomer in the presence of benzoyl peroxide as initiator under a dry N_2 atmosphere (section 2.4). This step was brilliant and let to increase the percentage efficiency of the PAAM-grafted-resin towards the metal ions rolling the water hardness, especially Ca^{++} and Mg^{++} ions, under investigation as shown in Table 3, and it reaches 83.68%, which may signify a breakthrough from the scratch consumed resin.

The obtained result is considered as an excellent ratio in comparison to those obtained with other monomers grafted on the consumed resin, that is, OABA, PABA, and AAM. This may be due to the chain length increasing of the AAM repeated unit, resulting in the improvement and increase of percentage efficiency of the grafted resin. It also gives an impression on the proficiency of the success of the grafting polymerization process, which allows more room to use the consumed resins, and it can be considered

as a positive step of chemical recycling which provides economic and environmental returns.

3.4.2. Hydrazine detection

The efficiency of the grafted resin towards hydrazine is examined by spectrophotometry technique. The advantages of spectrophotometry are acquired for its simplicity, availability, the old tradition of its application in analytical chemistry, and its providing of the required accuracy of hydrazine determination in these samples. Table 4 shows comparative efficiency results of removing hydrazine from boiler water sample between the consumed resin and its grafted resin using 0.06 mg/L as recommended by Mitsubishi Heavy Industries [32], who assembled the Hartha Power Station in Basrah where all the tested boiler wastewater samples are provided.

The efficiency is much higher in AAM and PAAM-grafted-resin 98.33% and 100%, respectively, and the lower efficiency was obtained with OABA and PABA grafted resin is 20 and 25 respectively, and un-grafted resin has the worst efficiency by 16.67%. These results are in good agreement with the results obtained from removing water hardness in terms of a sequence of the resin and grafted resin from an efficiency point of view.

It may be worth to mention here that the chemical grafting processes performed on the hard-consumed strong cationic resin have caused a change in some physical characteristics that affect the structure of granules, particularly, in their behavior under the grinding process, and the resin grafted with AAM is much easier to ground compared to the other grafted resin derivatives. This may open new applications as hardening or reinforcing materials.

Table 4

Efficiency of the consuming resin and its grafted derivatives with various monomers and polyacrylamide toward hydrazine

Resin	Concentration before treatment (mg/L)	Concentration after treatment (mg/L)	Efficiency (%)
Un-grafted resin	0.06	0.05	16.67
Resin-g-OABA	0.06	0.048	20.00
Resin-g-PABA	0.06	0.045	25.00
Resin-g-AAM	0.06	0.001	98.33
Resin-g-PAAM	0.06	0.0	100

4. Conclusions

OABA-g-resin, PABA-g-resin, AAM-g-resin, and PAAM-g-resin were synthesized by grafting consumed sulfonated polystyrene resin and have been characterized by an FTIR confirming that the three monomers and polyacrylamide have been grafted on the resin. All grafted resins were used for the removal of metal ions causing hardness in boiler wastewater samples. Removal of total hardness caused by metal ions Ca^{++} and Mg^{++} from industrial wastewater was best with the resin grafted with polyacrylamide, and it reached the highest efficiency of 83.68% among the other monomers used, and they are as follows; 55.37% for OABA-g-resin, 56.20% for PABA-g-resin, and 63.22% recorded for the AAM-g-resin, whereas ungrafted resin recorded only 54.34%. The grafted resin was also tested to remove the toxic hydrazine. Again, the resin grafted with polyacrylamide is the best with efficiency reaching 100%, and the nearest one to it is the resin grafted with acrylamide monomer with a recorded efficiency of 98.33%.

According to the results obtained, we suggest that polyacrylamide grafted resin serves best in removing hardness and the toxic hydrazine, which may, in turn; it can be used as an engorging-friendly material for wastewater purification.

References

- [1] F.Z. Al-Hamdani, Water pollution in Iraq between disastrous borders and no real solutions: a study, *J. Genet. Environ. Resour. Conserv.*, 1 (2013) 111–118.
- [2] R.H. Al-Suhili, Frequency analysis of some of water quality parameters of Shatt Al-Hilla River, Iraq, *Am. J. Eng. Res.*, 7 (2018) 190–199.
- [3] M.W. Henry, *Water Treatment: Principles and Design*, 2nd ed., John Wiley and Sons, Oxford, 2005.
- [4] C. Frayne, *Boiler Water Treatment, Principles and Practice*, Vol. 1, Chemical Publishing Co. Inc., United States, 2002.
- [5] T. Sato, F. Kimura, A. Kitoh, Projection of global warming onto regional precipitation over Mongolia using a regional climate model, *J. Hydrol.*, 333 (2007) 144–154.
- [6] O. Altansukh, G. Davaa, Application of index analysis to evaluate the water quality of the Tuul River in Mongolia, *J. Water Resour. Prot.*, 3 (2011) 398–414.
- [7] M.S. Moyel, N.A. Hussain, Water quality assessment of the Shatt al-Arab river, Southern Iraq, *J. Coastal Life Med.*, 3 (2015) 459–465.
- [8] M.A. Al-Marzok, H.S. Al-Lami, Iraqi Patent 3698 (27/11/2013).
- [9] A.A. Ansari, *Eutrophication: Causes, Consequences, and Control*, Vol. 2, Springer, New York, 2014.
- [10] WHO, *Environmental Health Criteria 68: Hydrazine*, World Health Organization, Geneva, Switzerland, 1987, pp. 1–89.
- [11] M. Sittig, *Handbook of Toxic and Hazardous Chemicals and Carcinogens*, 2nd ed., Noyes Publications, Park Ridge, New Jersey, 1985.
- [12] C.A. Almeida, S. Quintar, P. González, M.A. Mallea, Influence of urbanization and tourist activities on the water quality of the Potrero de los Funes River (San Luis – Argentina), *Environ. Monit. Assess.*, 133 (2007) 459–465.
- [13] S.O.H. Al-Shujairi, Develop and apply water quality index to evaluate the water quality of Tigris and Euphrates Rivers in Iraq, *Int. J. Mod. Eng. Res.*, 3 (2013) 2119–2126.
- [14] S.F. Pesce, D.A. Wunderlin, Use of water quality indices to verify the impact of Córdoba City (Argentina) on Suquía River, *Water Res.*, 34 (2000) 2915–2926.
- [15] Purolite Company, *Condensate Purification and the Influence of Operating Conditions on the Ion Exchange Processes*, U.K., 2010.
- [16] A.A. Mizhir, A.A. Abdulwahid, H.S. Al-Lami, Chemical functionalization graphene oxide for the adsorption behavior of bismarck brown dye from aqueous solutions, *Egypt. J. Chem.*, 63 (2020) 1679–1696.
- [17] M.T. Sultan, H.S. Al-Lami, A.H. Al-Dujali, Synthesis and characterization of alumina-grafted acrylic acid monomer and polymer and its adsorption of phenol and p-chlorophenol, *Desal. Water Treat.*, 150 (2019) 192–203.
- [18] K. Kaewtatip, V. Tanrattanakul, Preparation of cassava starch grafted with polystyrene by suspension polymerization, *Carbohydr. Polym.*, 73 (2008) 647–655.
- [19] U. Abdulganiyu, M.M. Saminu, M. Aminu, Graft copolymerization and characterization of styrene with chitosan via radical polymerization, *Chem. Search. J.*, 8 (2017) 56–63.
- [20] R.M. Islamova, O. Golovochesova, Y.B. Monakov, I.A. Utepova, A.A. Musikhina, O.N. Chupakhin, Effect of heterocyclic derivatives of ferrocene on free-radical polymerization of methyl methacrylate and styrene, *Polym. Sci. Ser. B Polym. Chem.*, 52 (2010) 637–647.
- [21] L.P. Krul, L.B. Yakimtsova, E.L. Egorova, Y.I. Matusevich, K.A. Selevich, A.L. Kurtikova, Preparation and thermal degradation of methyl methacrylate-methacrylic acid copolymers, *Russ. J. Appl. Chem.*, 82 (2009) 1636–1643.
- [22] Mitsubishi Standard, *Testing Methods for Boiler Feed Water and Boiler Water*, Technical Administration, Japan, 1979.
- [23] R.A.C. Lima, S.R.B. Santos, R.S. Costa, G.P.S. Marcone, R.S. Honorato, V.B. Nascimento, M.C.U. Araujo, Hardness screening of water using a flow-batch photometric system, *Anal. Chim. Acta*, 518 (2004) 25–30.
- [24] R. Kaveeshwar, V.K. Gupta, A new spectrophotometric method for the determination of hydrazine in environmental samples, *Fresenius J. Anal. Chem.*, 344 (1992) 114–117.
- [25] A.D. Smolenkov, I.A. Rodin, O.A. Shpigun, Spectrophotometric and fluorometric methods for the determination of hydrazine and its methylated analogues, *J. Anal. Chem.*, 67 (2012) 98–113.
- [26] A.A. Zagorodni, D.L. Kotova, V.F. Selemenev, Infrared spectroscopy of ion exchange resins: chemical deterioration of the resins, *React. Funct. Polym.*, 53 (2002) 157–171.
- [27] R.M. Silverstein, X. Francis, *Spectrometric Identification of Organic Compounds*, 6th ed., John-Wiley and Sons Inc., USA, 1997.

- [28] A.J.M. Al-Karawi, Z.H.J. Al-Qaisi, H. Ismael Abdullah, A.M.A. Al-Mokaram, D.T.A. Al-Heetimi, Synthesis, characterization of acrylamide grafted chitosan and its use in removal of copper(II) ions from water, *Carbohydr. Polym.*, 83 (2011) 495–500.
- [29] S.H. Mutasher, A.A. Salih, H.S. Al-Lami, Preparation of some chitosan derivatives and study their effect on human genetic material, *Der Pharma Chem.*, 8 (2016) 125–134.
- [30] A.G. Ibrahim, A.Z. Sayed, H.A. El-Wahab, M.M. Sayah, Synthesis of poly(acrylamide-graft-chitosan) hydrogel: optimization of the grafting parameters and swelling studies, *Am. J. Polym. Sci. Technol.*, 5 (2019) 55–62.
- [31] V. Singh, A.K. Sharma, R. Sanghi, Poly(acrylamide) functionalized chitosan: an efficient adsorbent for azo dyes from aqueous solutions, *J. Hazard. Mater.*, 166 (2009) 327–335.
- [32] Mitsubishi Standard, Hartha Thermal Power Station, Water Testing Procedures Manual, Mitsubishi Industries, Japan, 1980.