

Radiation Copolymerization of Styrene/Acrylic Acid Grafted to Silica Surface For separation and purification purposes:

I. Characterization and sorption of some organic compounds and Metals.

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Abstract

Interconnected styrene/acrylic acid-based materials were prepared by radiation-induced graft copolymerization of Styrene/Acrylic Acid onto surface of Silica prepared from rice husk ash in presence of dioxane as a solvent (SAAS). The influence of synthesis conditions was studied. It was found that the amount and the nature of the silica had profound influence on the properties of the polymer obtained. SAAS was characterized through water uptake (swelling), Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscope (SEM). Water uptake percent increases with the absence of styrene, decreasing AAc ratio and increasing of silica ratio in powder form in the initial feed solutions to reach 24174 (mol/gm) and this prepared copolymer has a considerable capacity for adsorption of organic compounds and metals. Sorption of some organic compounds; Methylene Blue (MB), P-Nitro Phenol (P-NP), Tartrazine (T) and Congo Red (CR) and heavy metals; Pb(II), Co(II), Ni(II), Sr(II), Fe(III), and Cr(III) ions onto SAAS adsorbents were investigated in aqueous condition. The sorption properties of the SAAS grafted copolymers recommend them as an alternative for other composite sorbents in the removal and separation of small ionic species like organic dyes and heavy metals from aqueous solution.

Key words: Radiation, Graft copolymers, Silica, Sorption, Organic compounds, Heavy metals.

Introduction

The pollution of water from toxic compounds, heavy metal ions and dyes imposes ecological and public problem due to hazardous and irrecoverable effects of such pollutants on human health and the environment [1-3]. Nowadays, a number of promising processes are used for elimination of heavy metal ions and dyes from wastewaters. Adsorption is a convenient separation process, in which the adsorbent may be of organic, mineral or natural source [4]. Various materials such as zeolites, activated carbon, clays, agricultural wastes, biomass and synthetic polymers were used as an adsorbent [5,6]. However, these sorbents suffer from several problems such as low mechanical and thermal stability, high cost and poor sorption capacity. It is well known that biopolymers which are abundant, biodegradable and renewable resources have a high capacity to bind with a variety of waste molecules or ions through chemical and physical interactions. Among them, polysaccharide type biopolymers such as cellulose, chitosan, cyclodextrin, sodium alginate (SA) have received more attention [7-9]. The radiation-induced graft copolymerization (RIGC) as a method of modification of polymeric materials has been extensively used over recent years. This is explained by the versatile and universal character of

the radiation induced grafting. This is one of the more accepted methods for the syntheses of advanced materials to be used in the field of medicine and biotechnology. The application of RIGC for obtaining biocompatible polymeric materials is of great importance. It is well known that the graft allows obtaining products with a wide range of properties. The radiation-induced graft copolymerization, started last century (1950) with continuous research efforts from different groups with a clear goal to obtain modified materials for diverse applications [10-13]. The main feature of interest is the potential to simplify the treatment process as a whole. Simultaneous irradiation method is the simplest irradiation technique for preparation of graft copolymers. In this method the polymer backbone is irradiated in the presence of monomer. Irradiation is carried out mostly in inert atmosphere or vacuum; sometimes the pre-irradiation method is used. In the latter method, the main chain of the polymer is irradiated to form active sites which act as macro-initiators; later the monomer reacts with these active sites of the irradiated polymer. To date, both techniques give grafted copolymers with improved properties and it is hard to decide which of them is better. Our research work is related with simultaneous irradiation methods through reasonably good results in the experimental conditions used. State of art report several works dealing with the RIGC's processes [10-14]. We are focused in the radiation induced graft copolymerization on styrene/acrylic acid onto surface of silica prepared from rice husk ash in presence of dioxane as a solvent. Our efforts are devoted to prepare various graft copolymers of gamma RIGC reaction. This was prompted by their great potential to be used in separation and purification purposes. The aim of the present work is to investigate the RIGC of monomers onto surface of silica prepared from rice husk ash in tow forms; gel and powder. This investigation is focused in the syntheses, characterization and application in the sorption of some organic compounds (dyes) and some heavy metals of an influence on the human health and environmental as a hole.

Materials and methods

The base silica: Preparation of silica from rice husk ash.

Rice husk ash (RHA), was prepared by carbonization of Rice Husk (RH) at 500°C for 1 hr. RHA was stirred with a solution of concentration 5% KOH at a weight ratio of 1:12 (g/ml) RHA to solution, respectively, and heated to boiling for 1 hr. Then, the mixture was left overnight, filtered and washed twice with distilled water at a weight ratio of 1:8. The filtrate was collected, and subsequently used, as it is predicted to contain leached silica which is the major component of the ash. To the filtrate, 10% HCl was added, until the pH of the solution reached 5-7, to form the silica gel. The obtained silica gel was used in two forms: the first is as it is in the wet form, and the second is after drying in an oven at 120 °C for sufficient time to the constant weight.

The monomer and reagents used:

The reagents used during copolymerization as monomers (styrene, acrylic acid) and different solvents (Sigma Aldrich), were used without any further purification.

Radiation induced grafting:

The base silica dissolved in sodium hydroxide solution were placed into glass tube and then grafting solution composed of monomer and solvent was added to the tube which were then purged with dry nitrogen for 30 minutes, subsequently sealed and then irradiated at Co⁶⁰ gamma irradiation cell. Grafting copolymerization reactions were carried out for certain times to achieve

reasonable grafting by irradiation dose. The addition of silica and different monomer and solvents were added according to the ratio 1:2:1 of styrene / acrylic/ dioxin to 2, 4, 6 of silica and 2, 3, 5 of silica solution in gel and powder form respectively. Also, Samples without styrene were prepared according to the ratio 0.7:1 of acrylic/ dioxin to 2,4,6 ml and 4,6,10 ml of silica solution in gel and powder form respectively. After dissolving and the addition of silica to the mixture of copolymer sty/AAc and dioxane solvent, the mixture was taken under vigorous steering then pebbling under nitrogen gas for 5-7 mints to extract oxygen and then exposed to irradiation dose of 20 KGy (1.2 Gy/second). Irradiation of samples was carried out at the National Center for Radiation Research and Technology, NCRRT (AEA), Nasr City, Cairo Egypt. The grafted copolymers were washed with the solvent used during grafting in order to remove residual monomer and/or polymer, which were not bonded to the base copolymer, then dried at 70 °C and reweighed.

Characterization of prepared copolymer:

- **Fourier transforms infrared spectroscopy (FTIR):** The structure of both the base silica and the grafted copolymers was analyzed by Fourier transform infrared (FTIR) spectroscopy. Measurements were carried out in absorbance mode in a wave range of 4000-500 cm⁻¹.

- **Scanning Electron Microscope (SEM):** Scanning Electron Microscope, SEM, (Supra 35VP, Leo, Germany) measurement were conducted to investigate the surface morphology the surface of the copolymer. An accelerating voltage of 10 kV was used during the measurements.

- **Swelling kinetics:** Swelling properties of the copolymers were studied using the conventional gravimetric procedure [15, 16]. To evaluate the swelling kinetics, the dried polymers were immersed in water at pH 5.5, and 25 °C. Swollen samples were weighed by an electronic balance, after wiping the excess surface liquid by filter paper. The swelling ratio (SR) was defined by following equation:

$$SR = (W_t - W_d) / W_d = g \text{ g}^{-1} \dots\dots\dots(1)$$

Where W_d is the weight (g) of the dried sample, and W_t is the weight (g) of the swollen sample, at time t .

- **Sorption from solution:** The different synthetic copolymers grafted to silica were tested for their feasibility to treatment of some organic compounds: Methylene Blue (MB), 4-Nitophenol (4-NP), Trartrazine (T) and Congo Red (CR). In addition to organic compounds some of metals such as: Pb, Sr, Ni, Co, Cr and Fe were used to investigate the efficiency of prepared copolymer for sorption of metal ions from aqueous solutions. A known volume and concentration of each organic and metal ions at its initial pH was mixed with known weight of each sample of prepared copolymer and shacked at room temperature for 24 hr. The residual concentration of each solution was measured using UV for organic compounds and Atomic Absorption spectrophotometer for heavy metals respectively. The uptake of each sample was measured using the following equation:

$$\text{Uptake} = (C_o - C_e) \times (V/M) \text{ (mg/g)}. \quad (2).$$

Where, C_o and C_e are initial and final concentrations of adsorbate. V is the volume of adsorbate solution (per liter) and M is copolymer sample weight in gram. And % removal calculated from the following equation:

$$\% \text{ Removal} = (C_o - C_e) \times (100/C_o). \quad (3)$$

Results and discussion

The results obtained in this work are discussed in three subsections. In the first subsections, the synthesis and characterization of grafted copolymers are presented. In the second and third

subsection the sorption and separation capacity of the copolymers against some organic compounds and some heavy metals which used in a different industrial field and scientific application have been investigated.

Characterization of prepared samples

- FTIR spectroscopy

FTIR is an important in studying the copolymer structure. The width and intensity of the spectrum bands, as well as the position of the peaks confirm the functional groups that take part in the formation of copolymer and the others that contribute in the sorption and removal of water pollutants. The IR spectra of copolymer in four different composition are shown in fig.(1a-d). Fig. (1a) shows the FT-IR spectra of copolymer of the styrene/acrylic acid/dioxane anchored on silica in gel form. Characteristic absorption bands were clearly visible at 3333 cm^{-1} corresponding to the -OH stretching vibrations, this band is due to the stretching vibrations of free -OH groups [17]. A band at 1239 cm^{-1} due to the -OH bending vibration and the band at 2937 cm^{-1} are attributed to the stretching vibration of -CH. The C-C and C-O stretching vibration was observed at 1137 cm^{-1} and 1091 cm^{-1} , respectively. The sharp band at 1722 cm^{-1} corresponds to the C=O stretching of the carbonyl group present in the networks. The corresponding bending and wagging of -CH vibrations is at 1422 cm^{-1} and 1327 cm^{-1} , respectively. In figure (1-b), as the amount of silica gel increased the absorption band decreased due to more reaction between the monomers and the silica. The band at 3333 cm^{-1} due to -OH stretching of carboxylic group overlapped with the -OH of silanol groups on the surface of the silica. Figure (1-c and d) describe approximately the same behavior of the copolymers prepared from silica in the powder form.

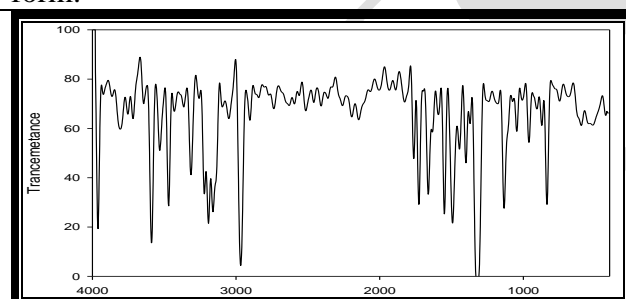


Fig.(1-A): FTIR spectra of copolymer prepared from 1:2:1 of styrene: acrylic acid: dioxane and 2 ml of silica in gel from(S₁)

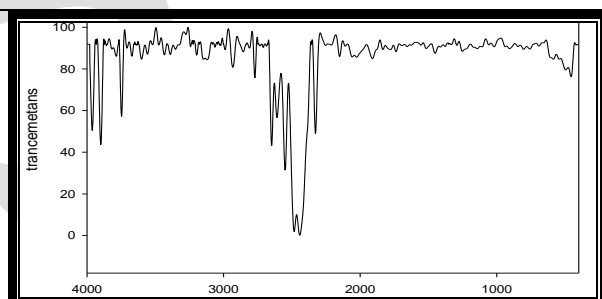


Fig.(1-B): FTIR spectra of copolymer prepared from 1:2:1 of styrene: acrylic acid: dioxane and 4 ml of silica in gel from(S₂)

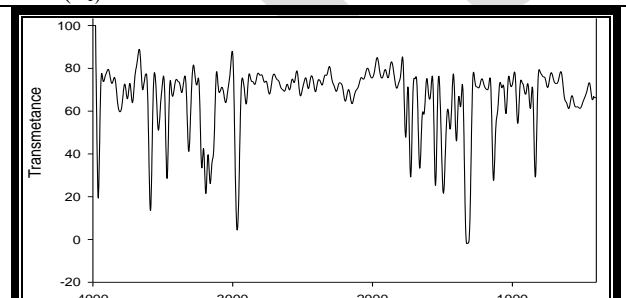


Fig.(1-C): FTIR spectra of copolymer prepared from 1:2:1 of styrene: acrylic acid: dioxane and 3 ml of silica in powder from(S₅)

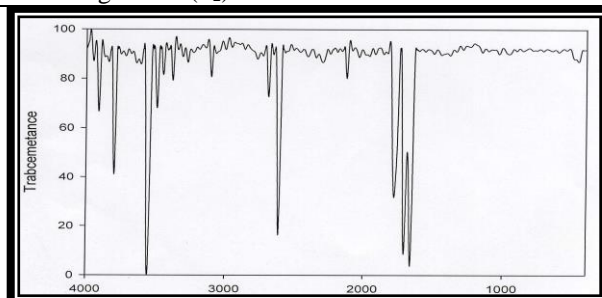


Fig.(1-D): FTIR spectra of copolymer prepared from 0.83:1 of acrylic acid: dioxane and 6 ml of silica in powder from(S₁₁)

Figure (1): The FTIR of four samples of the prepared grafted copolymer with different ratios of organic constituents and silica in gel and powder forms.

- *Scanning electron microscopy (SEM).*

It was used here to detect the topography of the copolymer grafted to silica gel surface before and after loading with Tartrazine and Congo red. The SEM observations of the copolymer sample of Silica (in gel form) grafted with Acc/styrene and the same copolymer loaded with tartrazine and Congo red is shown in figure (2a-b-c). The surface of the first sample was smooth, as seen in Figure 2(a). After loading with tartrazine and Congo red the surface became rough with a number of holes due to the accumulation of tartrazine and Congo red. The surface morphology of two samples are shown in the figure 2(b and c).

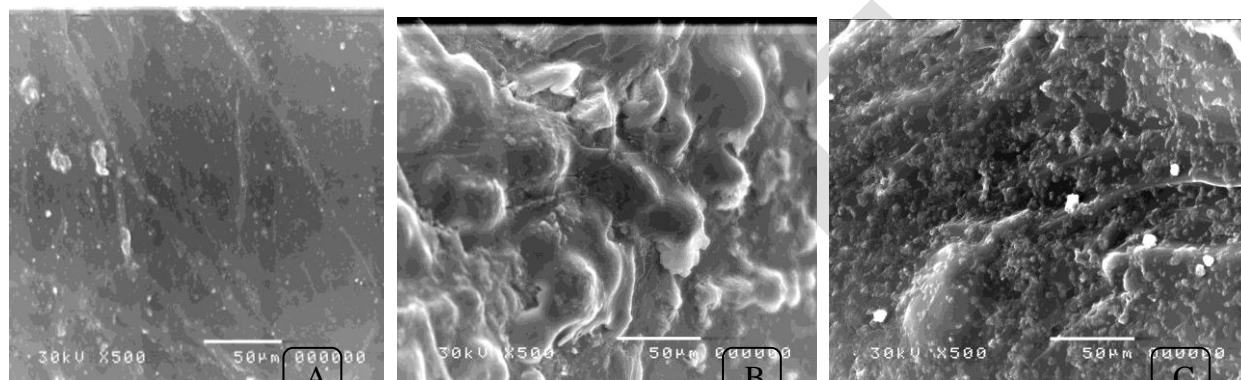


Figure (2): (A) SEM of copolymer prepared from styrene/acrylic acid/ silica in gel form, (B) loaded with Tartrazine, (C) loaded with Congo Red.

- *Swelling kinetics*

The capacity of swelling is one of the most important parameters that evaluating the properties of copolymer and hydrogels. Many structural factors such as; the charge, concentration, pKa of the ionizable group, degree of ionization, cross-linking density and hydrophilicity, influence the swelling of polyelectrolyte polymers, and the properties of the swelling medium like the pH, temperature, ionic strength, counter ion, and its valence affect the swelling characteristics [18]. The swelling ratio for different polymers at pH 7 was investigated and shown in Fig. 3.

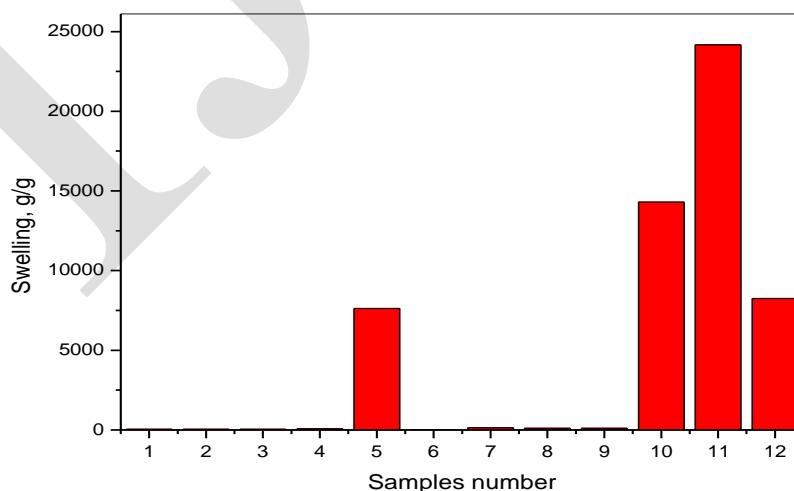


Figure (3): Swelling percent of the prepared copolymer in distilled water.

The figure shows the swelling capabilities of all investigated samples are increased with the absence of styrene and increase of silica in powder form up to the ratio AAc: dioxane : silica

of 0.83:1:2. The increase of silica in presence of AAc content would result in enhancing the number of ionizable groups which increase the electrostatic repulsions, whatever; an increasing in the swelling ratio was occurred. The same behavior was observed by many other studies [19]. The swelling of polymer can be also affected by pH and temperature of the swelling media [20]. The pH-responsive swelling behavior is basically due to ionization of the functional groups in the polymer, which depends on the pH of the surrounding medium.

Table (1): Structures of the constituents of the prepared grafted copolymers.

Styrene	Acrylic acid	Dioxane	Silica Gel
C_8H_8 Poly(1-phenylethylene)	$CH_2=CHCO_2H$ Poly(acrylic acid)	$C_4H_8O_2$ 1,4-Dioxane	 Silica Gel

The following table explains the ratio of the copolymer components and the swelling properties of the obtained copolymers.

Table 2: Preparation of different types of copolymers using different forms of silica.

Sample s No.	Styrene	AAC	Dioxane	Silica		Swelling %
1	3 ml	6 ml	3 ml	2 ml	- Gel form	51.15
2	3 ml	6 ml	3 ml	4 ml		51.97
3	3 ml	6 ml	3 ml	6 ml		51.47
4	3 ml	6 ml	3 ml	2 ml	- Powder form	70.86
5	3 ml	6 ml	3 ml	3 ml	[0.2 gm of silica + 10 ml 1N NaOH]	7626
6	3 ml	6 ml	3 ml	5 ml		19.60
7	--	2.5 ml	3 ml	2 ml	- Gel form	134.9
8	--	2.5 ml	3 ml	4 ml		100.4
9	--	2.5 ml	3 ml	6 ml		108.8
10	--	2.5 ml	3 ml	4 ml	- Powder form	14305
11	--	2.5 ml	3 ml	6 ml	[0.4 gm of silica + 20 ml 1N NaOH]	24174
12	--	2.5 ml	3 ml	10 ml		8254

Adsorption of some organic compounds

The following table (3) shows the percent removal and uptake (mg/g) of Methylene Blue, P-Nitro Phenol, Tartrazine and Congo Red at different adsorbent dose and pH values according to the preparation condition of each sample.

Adsorption of Methylene Blue Using prepared copolymer

Methylene blue (CI 52015) is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. It has many uses in a range of different fields, such as biology and chemistry. As reported in literature, the ionic dyes are used as models for drugs in preliminary tests for controlled drug release from various supports [19, 20]. Furthermore, finding novel, cheaper and highly efficient sorbents for the removal and separation of small ionic species like organic dyes from aqueous solution is one of the most stringent tasks [21-23]. The possibility to adsorb cationic dyes onto copolymers has been investigated. From the following table (3) it is clear that: The presence of styrene in preparation of copolymer from silica in gel form decrease the % removal of MB. On the contrary, the presence of it in preparation of silica in powder form increases the % removal of MB and as the concentration of silica increases the % removal increased. Generally, the obtained results indicated that the highest % removal did not depend on the presence or absence of styrene in the preparation of copolymer and the silica is in gel or powder form. And the best result was obtained using sample 6 and 7 as seen from table (3). The absence of styrene in the preparation of copolymer from silica in powder form leads to the increase of swelling % but there is no relationship between the swelling and % removal of MB. Finally, Starting weight of the samples and pH of the MB after mixing with copolymer had no effect on the % removal of MB from solution.

Adsorption of P-NitroPhenol.

Phenolic compounds occur frequently in the aquatic environment through [24, 25]: (i) direct discharge of industrial wastewaters containing dyes, herbicides, surfactants, etc.; (ii) effluents from oil refineries and olive mills; (iii) effluents from the plastics, leather, paper, paint, pharmaceutical and steel industries. Phenolic compounds cause an unpleasant taste and odour (even at low concentrations) in drinking water, and can exert negative effects on different biological processes [26]. Most of these compounds are recognized as toxic carcinogens to humans and aquatic life and need to be eliminated for safe discharge [24]. The European Union and US Environmental Protection Agency (USEPA) have placed phenol and its derivatives (e.g. nitrophenols and chlorophenols) on their priority pollutants lists [27]. Adsorption appears as the best technique to remove phenols at low concentration. Especially phenol is widely taken as a reference compound for adsorption capacity determination [28]. The adsorption capacity of any adsorbent depends on [9]: (a) the nature of the adsorbent (e.g. functional groups present, surface area and pore size distribution, ash content); (b) the nature of the adsorbate (e.g. surface functional groups, polarity, hydrophobicity, molecular weight and size, solubility and pKa); and (c) the solution conditions (e.g. pH, temperature and adsorbate concentration, presence of competitive solutes, polarity of solvent). The prepared copolymer was used for adsorption of PNP and the % removal was summarized as shown in the above table. From this table: The presence of styrene in preparation of copolymer from silica in gel form decrease the % removal of PNP. But, the presence of it in preparation from silica in powder form increases the % removal and as the concentration of silica increased the uptake decreased whereas in absence of styrene, as the concentration of silica increases the % removal of PNP reaches 100 %. The results indicated that the highest % removal was obtained by sample 12 as shown from table (3). The

results showed that there is no relationship between weight of the samples and % removal of PNP. pH of the solution play an important role in the % removal where, as the pH of solution increased the % removal increased and the highest value of % removal (100%) was obtained at pH = 6.18.

Table (3): Adsorption of MB, P-NP, Tartrazine and Congo Red using prepared copolymers.

No	MB	P-NP	Tartrazine	Congo Red
Structure				
	Start weight	Start weight	Start weight	Start weight
1	0.0967	0.1056	0.1139	0.0525
2	0.0997	0.0926	0.0972	0.0652
3	0.1028	0.1139	0.1051	0.0570
4	0.1131	0.1163	0.0912	0.0684
5	0.1047	0.1005	0.1010	0.0517
6	0.0972	0.1111	0.0962	0.0631
7	0.0960	0.0921	0.1176	0.0716
8	0.1111	0.1072	0.1107	0.0733
9	0.1054	0.1110	0.1118	0.0736
10	0.1108	0.1045	0.0902	0.0639
11	0.1047	0.1084	0.1108	0.0714
12	0.0971	0.0913	0.1115	0.0631
TC	179.56	180.43	12.211	762.44
	Swilli ng %	q _e (mg/g)	%R	%R
1	82.52	5.673	1.43	52.3
2	78.13	8.341	..	100
3	51.16	4.723	1.1	100
4	26.79	17.094	21.5	100
5	6094.8	18.364	12.8	..
6	5558.4	20.098	6.83	18.8
7	88.54	20.062	0.16	8
8	69.66	17.396	0.9	100
9	81.78	18.360	4.13	100
10	9502.8	17.357	11.4	..
11	15276	16.047	82.0	..
12	17190	16.04	100	..
TC		180.43		762.44
	pH	%R	q _e mg/g	q _e (mg/g)
1	3.88	27.43	1.765	74.777
2	3.72	41.58	2.93	115.03
3	3.8	24.28	..	131.578
4	4.18	96.67	7.88	109.649
5	5.3	96.14
6	5.34	97.68	..	22.441
7	3.6	96.3	4.13	104.748
8	3.5	96.64	6.73	102.319
9	3.45	96.76	9.46	101.902
10	5.35	96.16
11	6.00	84.01
12	6.35	77.7
TC		179.56		762.44
	TC	TC	TC	TC
1	83.232	344.61	246.74	375.2
2	124.35	344.61	246.74	375.2
3	137.03	344.61	246.74	375.2
4	143.25	344.61	246.74	375.2
5	28.34	344.61	246.74	375.2
6	75.149	344.61	246.74	375.2
7	126.33	344.61	246.74	375.2
8	122.60	344.61	246.74	375.2
9	126.29	344.61	246.74	375.2
10	25.56	344.61	246.74	375.2
11	98.37	344.61	246.74	375.2
12	82.14	344.61	246.74	375.2
TC		344.61	246.74	375.2

[For MB: C₀= 100 mg/l, V = 20 ml, pH₀ = 3.9, for PNP: C₀= 300 mg/l, V = 25 ml, pH₀ = 4.71, For tartrazine: C₀= 150 mg/l, V = 25 ml, pH₀ = 6.18 and for Congo red: V=30 ml, C₀=250 mg/l, pH₀= 6.15].

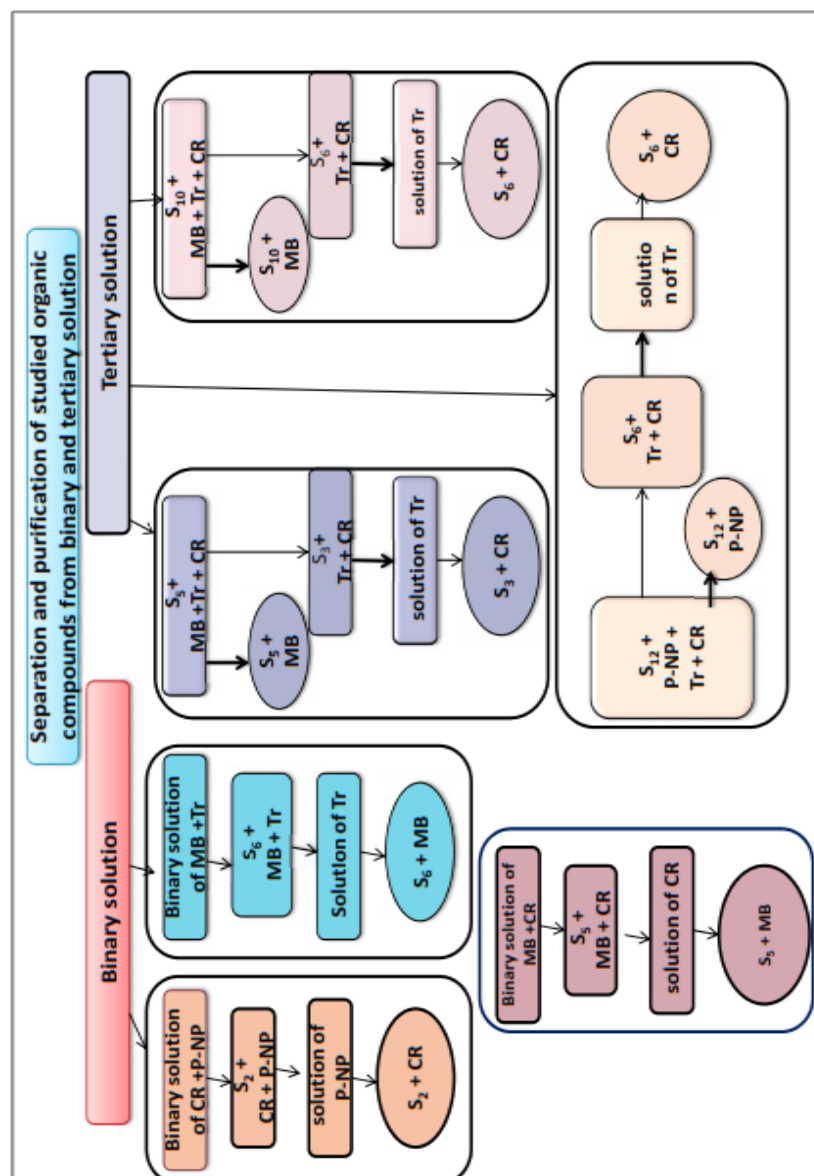


Figure (4): Schematic diagram of prepared samples for separation and purification purposes of some organic compounds.[MB: Methylene blue, P-NP: P-NitroPhenol, Tr: Tartrazine and CR: Congo Red].

Adsorption of tartrazine

The dye under investigation, Tartrazine (otherwise known as E102 or FD&C Yellow 5) is a coal-tar derivative that is used to colour foods, cosmetics, and other products, it is a lemon yellow azo dye used as a food colouring. It is found in certain brands of fruit squash, fruit cordial, coloured fizzy drinks, instant puddings, cake mixes, custard powder, soups, sauces, ice cream, ice lollies, sweets, chewing gum, marzipan, jam, jelly, marmalade, mustard, yoghurt and many convenience foods together with glycerine, lemon and honey products [29]. It is cheaper than beta carotene and therefore used as an alternative to beta carotene to achieve similar colour. The water-soluble Tartrazine is used in drugs especially shells of medicinal capsules, syrups and cosmetics. Tartrazine is a yellow menace, whose wide use in industry and its water-soluble

nature maximize its chances to be found as contaminant in industrial effluents. Tartrazine is also reputed to catalyze hyperactivity [29] and other behavioral problems, asthma, migraines, thyroid cancer [30], etc. Because of its hazardous health effects, foods and drinks containing Tartrazine are avoided. The present study is devoted to its removal from the wastewater using adsorption technique. The study has been carried out using the prepared copolymers. As seen from table (3), the tartrazine has a high molecular size which may decrease the mobility of it through the steps of the adsorption processes leading to the decrease of the adsorption process of such molecules. There is no relationship between sample weight and uptake. The presence of silica in powder form in absence of styrene leads to the prevention of uptake completely. The presence of silica in gel form and in absence of styrene in copolymer makes the uptake of Tartrazine is better than in presence of styrene.

Adsorption of Congo Red (CR)

Congo red is the sodium salt of 3, 3'-([1, 1'-biphenyl]-4, 4'-diyl) bis (4-aminonaphthalene-1-sulfonic acid)(formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol). It is a secondary diazo dye. Congo red is water soluble, yielding a red colloidal solution; its solubility is better in organic solvents such as ethanol. Due to a color change from blue to red at pH 3.0-5.2, Congo red can be used as a pH indicator. As seen from the table (3), the starting weight of the sample had no effect on the percent removal of CR using prepared copolymer. In absence of styrene through preparation of copolymer from silica gel is recommended and leads to 100% removal of CR whereas preparation from silica powder leads to 0.0 % removal of CR. In presence of styrene, preparation of copolymer from silica in gel form is also preferred than silica in powder form and leads to higher % removal. pH of the solution has no effect on the % removal of CR using prepared copolymer.

Adsorption of heavy metal.

Pollution caused by the presence of metal ions is assuming dangerous proportions as toxic metal ions are present in most of the water discharged from industries, mining effluents and municipal wastes. They are not biodegradable and can accumulate in living organisms [31]. Therefore, these heavy metals can be considered as one of the most important pollutants for waters and waste waters [31]. As industry expands, heavy metal ion contamination is exacerbated. When heavy metal ions are assimilated into living organisms, they accumulate in living bodies, causing serious diseases even at very low concentrations. Therefore, many separation methods have been developed for removing heavy metal ions from aqueous solutions, including reduction and precipitation, coagulation, reverse osmosis, electrodialysis, and adsorption [32]. Among these technologies, adsorption of heavy metal ions using chelating resins is highly popular because they are reusable, easy to handle and have higher adsorption efficiencies and selectivity. Poly acrylic acid polymer is choice as a hydrogel material, it shows a very high hydrophilicity and its pendant carboxylic group acts as efficient anchor for the polar and ionic species. Also, these hydrogels are highly susceptible to variation in pH and ionic nature of the medium, this enables it to use as ion exchangers [31]. With regard to the degree of functionalization, the transformation of poly styrene into cation exchange polymer can be accomplished by several methods. Hegazy et al. used radiation synthesized and well characterized poly (N-vinyl-2-pyrrolidone/acrylic acid) and poly(N-vinyl-2-pyrrolidone/acrylamide) hydrogels for the separation and extraction of some heavy-metal ions from waste water [33]. In view of the above, we have attempted to prepare hydrogels by graft copolymerization of acrylic acid, styrene onto silica extracted from rice husk ash via radiation to

act as polymeric adsorbents for metal ions such as Pb^{2+} , Sr^{2+} , Ni^{2+} , Co^{2+} , Cr^{3+} and Fe^{3+} from aqueous solution. As seen from table (4), the total adsorption capacity of prepared copolymer toward the studied heavy metal take the following order: $\text{Pb}^{2+}(524.4) > \text{Ni}^{2+}(506.1) > \text{Sr}^{2+}(496.3) > \text{Fe}^{3+}(273.9) > \text{Co}^{2+}(237.5) > \text{Cr}^{3+}(8.239)$ mg/g.

Adsorption of Pb^{2+} ions.

Lead poisoning causes damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnant women [34]. In this respect, wastewater containing heavy metals especially lead must be dealt with before being discharged. Recently, the applications of copolymer microparticles and nanoparticles or hydrogels with crosslinked three-dimensional network structure as adsorbents for adsorption of heavy metal ions and ammonium nitrogen have drawn considerable attention. Compared with other adsorbents, hydrogel possesses lots of functional groups and unique network structure, and so it could adsorb and trap metal ions or ionic dyes from effluents more efficiently [35]. In our study, the form of silica used in the preparation of the copolymer has a great effect on the adsorption capacity of the copolymer obtained. In both cases of presence and absence of styrene the copolymer prepared from silica in powder form has a higher adsorption capacity than those obtained from silica in gel form. This may be due to: increase of the swelling in case of powder form than in the gel form leading to increase of surface area available for removal of Pb^{2+} ions, increase of pH of the adsorption medium in case of powder form than in gel form leading to the increase of negative charge of the copolymer enhancing the higher adsorbability of the positive metal ions. A more acidic medium leads to a lesser amount of metal removed. For the pH values lower than the pKa values of the chemical groups present in the copolymer (pH usually between 4.0 and 6.0), there may be strong competition between H^+ ions and metal cations for the adsorption on active sites. This competition leads to a significant decrease in the amount of Pb^{2+} ions removed. The best pH range for the removal of Pb^{2+} ions was between 4.5 and 5.5. The presence of styrene decreases the pH and swelling of the copolymer and consequently, the uptake of Pb^{2+} . However, the prepared adsorbents have the highest uptake of Pb^{2+} (524.4 mg/g) than the other studied heavy metal ions.

Adsorption of Ni^{2+} ions.

Nickel is one of the heavy metals of environmental concern. Nickel toxicity to humans has received intensive attention due to its carcinogenic behavior [36]. Conventional methods for removing heavy metals from aqueous solutions in industrial wastewaters include several techniques but most of these methods are expensive or generate harmful wastes. In our study, in the case of adsorption of Ni^{2+} the pH of the solution is lower than that of Pb^{2+} solution leading to the decrease of swelling of prepared copolymer and consequently the decrease of the uptake of Ni^{2+} (506.1 mg/g). Also, the presence of silica in powder form increase the uptake than in the gel form and the presence of styrene decrease the uptake of Ni^{2+} ions from aqueous solution.

Adsorption of Sr^{2+} ions.

In the nuclear industry, radioactive waste contains a variety of radionuclides, which will severely pollute the environment if the pollutants are not treated well. Strontium, especially radioactive ^{90}Sr , is one of the most frequently found radionuclides in the soil and groundwater at nuclear weapon test sites and nuclear waste repositories [37]. In addition, because of the chemical similarity to calcium, Sr^{2+} can easily replace Ca^{2+} in human bodies and cause anemia,

leukemia, as well as other chronic illnesses. Hence, it is very important to concentrate and separate the Sr(II) ions from the waste solutions. Treatment of liquid wastes is needed to convert the waste to a more stable solid form to decrease its volume. Among typical methods for waste water treatment, adsorption with solid adsorbents is an effective method because it is highly efficient and convenient to handle. In this study, the adsorbability of prepared copolymer is based on the swelling of prepared copolymer. As the swelling increase, the adsorption of Sr^{2+} increase. As in the case of the Pb^{2+} and Ni^{2+} ions, the powder form of silica is preferred in the preparation of copolymer and the absence of styrene leads to the increase of Sr^{2+} ions adsorbed. The pH of the adsorption medium plays an effective role in the adsorption of Sr^{2+} from solution. Because cation-exchange is the main reason for the adsorption of Sr(II) ions into adsorbents with carboxyl groups [6], metal cations other than Sr(II) ions in the system will baffle the adsorption behavior. When pH is low, the plentiful H^+ in the solution will compete with Sr(II) ions to combine with $-\text{COO}^-$ groups:



Thus, the strong acidity results in replacing the adsorbed Sr(II) ions by the H^+ , which will decrease the adsorption capacity of Sr(II) ions. Increasing the pH of the medium will increase the hydrolysis of polymer in aqueous solution, and provide more combining points to Sr(II) ions, which increases the adsorption capacity.

Adsorption of Fe^{3+} ions.

Iron is an important metal for all living organisms, and is required for respiratory pigments, proteins and many enzymes. Compared with other nutrients, iron availability is of increasing interest because it may limit primary production in the oceans and some natural lake waters. Acquisition of iron by phytoplankton is strongly influenced by iron speciation in natural water, while the iron uptake rate of phytoplankton is generally related to the computed equilibrium concentration of Fe(III) in natural water and is actually dependent on the concentration of dissolved inorganic Fe(III) species [39]. The uptake of Fe^{3+} (273.9mg/g) using the prepared copolymer is less than that of Pb^{2+} , Ni^{2+} , and Sr^{2+} . There is no any uptake of Fe^{3+} using copolymer prepared from silica in gel form in both cases of presence and absence of styrene. But, with the use of silica in powder form in presence of styrene has a considerable uptake of Fe^{3+} ions from solution.

Adsorption of Co^{2+} ions.

As an indispensable element for human's body, Cobalt (Co^{2+}) played a vital role in immune system, however, excessive intake could cause serious health problems. Polycythemia, diarrhea, nasopharyngitis and gastrointestinal disorders have been proved to have a close relationship with inappropriate Co(II) assimilation. Thus, the removal of Co(II) from aqueous solution is significant for public's safety[40]. As seen from table (40); the highest uptake of Co^{2+} (62.73 mg/g) was obtained by sample no. 11 which is composed of AAc grafted on the surface of silica in the powder form at pH =4.88 and swelling % of 4773. Decrease of silica ratio than the sample no.11 (sample no. 10) leading to the decrease of swelling % (2133) and increase of silica (sample no. 12) also increase the swelling % (9609), but in both cases the uptake of Co^{2+} is lower than the sample no.11. As in the above metals, the use of silica in gel form whatever in presence or absence of styrene decrease the uptake of Co^{2+} . The presence of styrene in the polymerization and grafting of acrylic acid on the surface of the silica in powder from decrease the uptake of

Co^{2+} . pH of the adsorption medium seems to have slight effect on the uptake of Co^{2+} , as the pH increase the uptake increase within the range below the pH of precipitation of Co^{2+} (pH > 8.5).

Table (4): Absorbability of prepared grafted copolymer toward some heavy metals.

Metal	Samples no.	1	2	3	4	5	6	7	8	9	10	11	12	TC
Pb^{2+}	$C_i = 200$	2.63	5.71	7.10	22.19	90.91	73.64	52.52	46.12	50.46	88.18	60.72	24.22	524.4
	mg/l	82.74	82.29	76.54	43.92	1676	2367	67.92	45.87	46.85	8081	11026	17657	
	pH _i =5.15	3.58	3.47	3.48	3.38	4.51	4.55	3.14	3.08	3.05	4.73	5.48	5.86	
Ni^{2+}	$C_i = 200$	32.03	--	29.70	35.68	81.63	66.80	5.49	18.35	6.31	67.61	75.19	87.26	506.1
	mg/l	74	61.52	130	78.73	400	485	55.89	118	147	1734	4364	6348	
	pH _i =5.92	3.61	3.52	2.94	3.31	3.83	3.85	3.01	3.04	3.05	4.08	4.52	5.01	
Sr^{2+}	$C_i = 200$	2.29	6.435	4.879	13.86	30.94	50.15	23.96	25.70	24.80	110.1	107.9	95.24	496.3
	mg/l	53.86	66.53	54.96	57.84	805.6	1186	105.9	94.6	120.3	3813	10787	14969	
	pH _i =5.73	3.59	3.50	3.62	3.35	4.21	4.20	3.00	3.03	3.05	4.46	4.97	5.56	
Fe^{3+}	$C_i = 200$	--	--	--	--	19.685	29.00	--	--	--	56.11	78.29	90.88	273.9
	mg/l	47.12	52.12	50.61	51.01	67.49	83.51	86	79.69	91.62	70.69	125.3	231.9	
	pH _i =2.39	1.99	1.96	1.92	1.97	1.96	2.02	1.97	1.97	1.98	2.04	2.11	2.38	
Co^{2+}	$C_i = 200$	--	1.93	--	7.94	34.49	27.54	5.59	3.68	2.00	44.29	62.78	47.21	237.5
	mg/l	40.31	74.03	29.84	56.18	663.02	567.8	128.12	102.7	102.8	2133	4773	9609	
	pH _i =6.46	3.95	3.64	3.93	3.71	4.22	4.23	3.37	3.36	3.38	4.34	4.88	5.27	
Cr^{3+}	$C_i = 200$	1.393	1.029	1.248	0.976	--	--	1.41	0.965	1.218	--	--	--	8.239
	mg/l	57.01	95.44	72.75	62.02	4317	4922	107.4	83.46	103.4	9553	17519	14604	
	pH _i =4.5	3.65	3.51	3.64	3.75	4.7	4.73	3.22	3.2	3.26	4.94	5.6	5.88	
Total Capacity		38.34	15.10	42.93	80.65	257.66	247.13	88.97	94.82	84.79	366.3	384.88	344.8	
			96.37			585.44			268.58			1095.98		
Condition of preparation		Styrene + AAc + silica gel			Styrene + AAc + silica powder			AAc + silica gel			AAc + silica powder			

TC: Total Capacity, C_i = initial concentration of metal ions solution, pH_i = initial pH of the prepared solution.

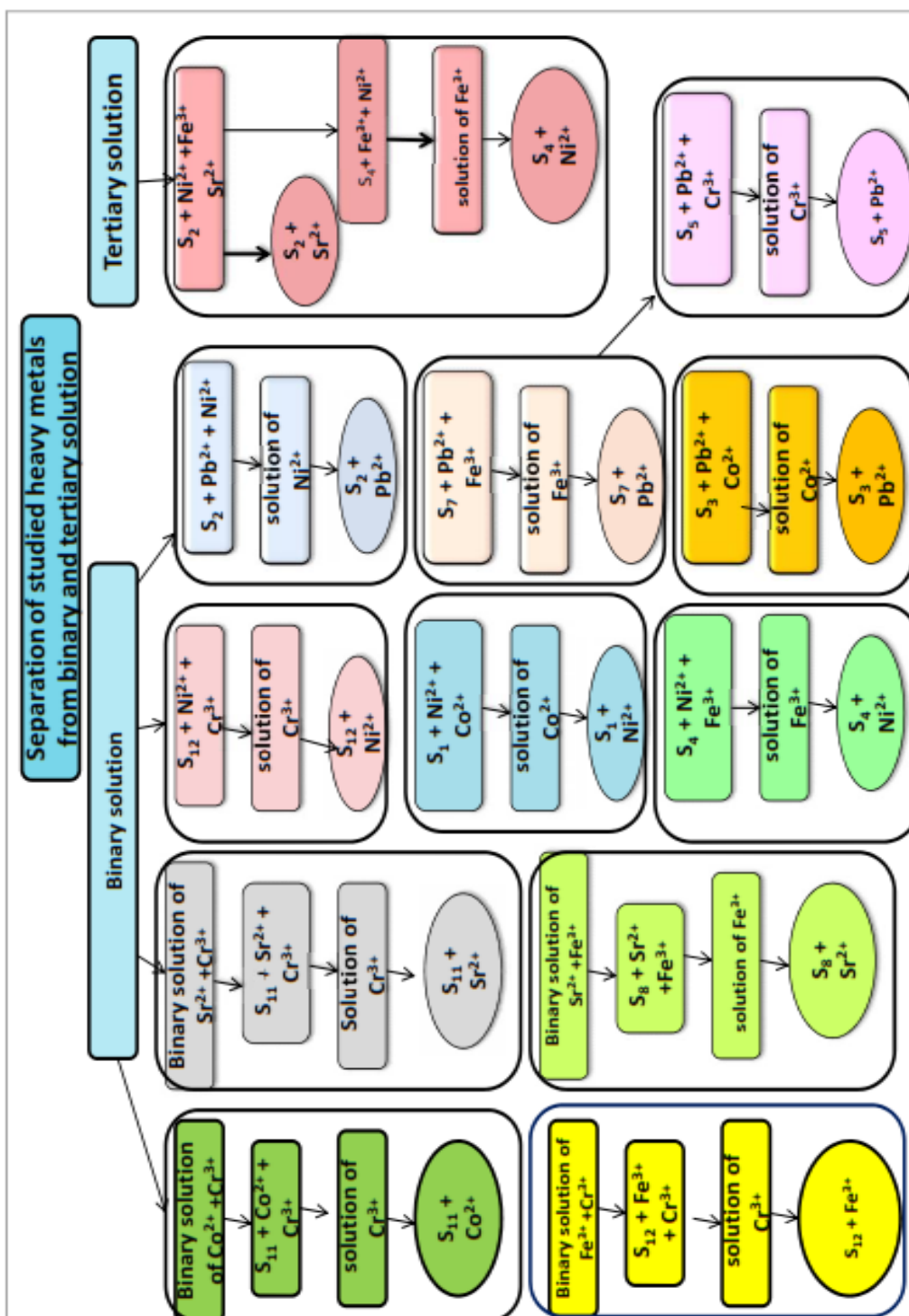


Figure (5): Schematic diagram of prepared sample for separation and purification purposes of some heavy metal ions.

Adsorption of Cr^{3+} ions.

Chromium is widely used in various industries, including electroplating, leather tanning, textile dyeing and metal finishing. In general, chromium exists in natural water in two oxidation states, the trivalent Cr(III) and hexavalent Cr(VI) states[41]. Chromium (VI) is 500 times more

toxic than the Cr(III) form. Human toxicity caused by Cr(VI) includes skin irritation to lung cancer; more specifically, it includes damage to the kidneys, liver and gastric tract. Because of its high toxicity, Cr(VI) must be removed from wastewater before being discharged to the aquatic system. In this study, the adsorption of Cr^{3+} take a reverse behavior than the other studied metals with respect to the preparation of polymer from silica in the powder form. Although the higher swelling % of the samples prepared from silica in powder form (and also all the prepared samples) there is approximately no any uptake of Cr^{3+} from the solution using samples no.10, 11 and 12. Therefore, generally, the Cr^{3+} has the lowest uptake (8.239 mg/g) of the concerned heavy metals. The preparation of polymer grafted to silica in gel form is preferred than the grafting to silica in powder form as seen from the table (4). pH has slight effect on the uptake of Cr^{3+} where as the pH decrease, the uptake of Cr^{3+} increase.

Future directions and recommendations

The constant growth in the demands for new functional polymers to meet the diverse challenges of separation and purification applications is driving renewed and fast growing interest in radiation-grafted materials and their versatile methods of preparation (RIGC: Radiation induced graft copolymerization). This is indicated by the rise in the number of related research projects in many research institutes. The International Atomic Energy Agency (IAEA) has coordinated a number of international R and D projects involving various countries aiming at developing new radiation-grafted materials for various industrial separation applications. The emphasis was dedicated to the development of new functional adsorbents and membranes and exploring new applications. To promote the application of the technology of radiation processing of polymers in general and RIGC in particular in industrial uses there is an immediate need to encounter the direct challenges hampering the technology spreading and limiting its product applications using multidisciplinary strategies. This includes; (1) development of new radiation-grafted materials for specific applications providing more tolerance to separation challenges than the conventional ones, (2) development of viable processes to produce radiation-grafted materials on a large scale, (3) development of new finished products/processes to utilize the materials and relevant technology and (4) extension of the applications boundaries of the known radiation-grafted materials to new areas of industrial interest. To achieve such goals, publicizing this technology among scientists and engineers working in the field of polymeric materials and membrane technology through education that involves short courses, hands-on training and group discussions is highly needed. This should coincide with activities enhancing public awareness and technology acceptance in the society [42].

Conclusion

From this study of preparation and characterization of copolymer of styrene and acrylic acid grafted on the surface of silica extracted from agricultural by-product rice husk in the two form gel and powder, it can be concluded that:

- Silica extracted from rice husk ash is a promising material that can be used in the preparation of radiation induced grafted copolymerization on the surface of it either in the gel or in the powder form.
- The presence of styrene has a tangible impact in the treatment of studied organic compounds in case of preparation of copolymer from silica in powder form. But it has a negative effect on the obtained adsorbent in the treatment of some heavy metals investigated in our study.

- pH of the initial solution of organic compounds did not affect greatly on the uptake of the studied organic compounds. In case of heavy metal, pH (below the precipitation limit of each metal) has a slight effect on the adsorption of studied heavy metals as the adsorption increase with the increase of pH.
- The uptake of the prepared samples toward organic compounds takes the following order: $375.159 > 344.612 > 246.739 > 206.07$ mg/g according to the preparation condition which are: AAc + silica in gel form > AAc+ styrene + silica in gel form > AAc+ styrene + silica in powder form > AAc + silica in powder form. i.e. silica in gel form is preferred in the preparation of adsorbent for treatment of organic compounds especially in absence of styrene.
- The adsorbability of organic compounds is independent of the size of organic molecules where it takes the following order: $762.44 > 180.43 > 179.56 > 12.211$ mg/g for Congo Red, P-NitroPhenol, Methylene Blue and Tartrazine respectively.
- The uptake of the prepared adsorbents toward heavy metal ions takes the following order: $1095.98 > 585.44 > 268.58 > 96.37$ mg/g according to the preparation condition which are: AAc + silica in powder form > AAc + styrene + silica in powder form > AAc + silica in gel form > AAc + styrene + silica in gel form. i.e. silica in powder form is preferred in the preparation of adsorbent for treatment of heavy metal ions, also, especially in absence of styrene.
- According to the adsorbability and the values of uptake obtained in our study, the prepared samples can be used in the separation and purification of organic compounds and heavy metals from binary and tertiary mixture of studied organic compounds and metal ions.
- There is no relationship between the swelling of the samples and their adsorption uptake.

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