

# Removal of Water Hardness and Some Inorganic Pollutants using Nano Marine Algae Extract Embedded in Waste Polystyrene

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**Abstract-** The capability of modifying synthetic resin (MSWPS) prepared from waste polystyrene plastics to remove hardness and some inorganic pollutants from synthetic hard water was investigated in this study. The waste polystyrene (WPS) was prepared from the foam of food packaging and white coffee cups, and then active adsorbent cationic resin was synthesized from them, forming sulfonated waste polystyrene (SWPS). The first preparation for hard water was made by dissolving  $MgCl_2$  or  $CaCl_2$  salts in deionized  $H_2O$  (DW) and passing it through SWPS resin to study the performance evaluation of the flow rate (mL/min), resin dosage (g), temperature ( $^{\circ}C$ ) and pH on the removal percentage of calcium, magnesium, and total hardness from this hard water. The efficient removal of water hardness and some inorganic pollutants was done using different concentration safety nano marine algae extracts (*Ulva fasciata*) embedded in SWPS then passing the second prepared hard water through the MSWPS resin. After adding nano marine algae extract (*Ulva fasciata*) to the (SWPS), the started removal efficiency of water hardness (1323 mgCaCO<sub>3</sub>/L), Ca<sup>2+</sup>, Mg<sup>2+</sup> ions (200mg/l) increased from (80% to 85%) for water hardness, (66% to 88.5%) for Ca<sup>2+</sup> ions, and (61.6 to 80.5%) for Mg<sup>2+</sup> ions respectively.

**Index Terms-** "Inorganic Pollutants, Nano Marine Algae, Removal efficiency, Water Hardness, Waste polystyrene"

## I. INTRODUCTION

Hard water (HW) can cause problems in heating and cooling systems, steam generation, and manufacturing in industrial chemical production and food processing (Gray, 2010 and Klemes, 2008). Drinking very hard water can cause cardiovascular problems and kidney stones due to the presence of unfavorable high concentrations of hardness. Hardness concentrations in natural water are up to 100mgCaCO<sub>3</sub>/L, depending on the associated sources, and are present in the range of 10-500mgCaCO<sub>3</sub>/L in drinking water (Pentamwa et al, 2011).

The problem of using HW directly without treatment may cause: salty deposits that lead to corrosion of metals; increased detergent demand when used for laundry; longer time required for cooking, etc. The most effective method for removing selective ions from groundwater is the ion exchange process using synthetic resins and natural materials. The most effective method for removing hardness at the household level is by using the boiling method (Schaep et al, 1998). The ion exchange resins have different commercial and industrial uses, especially in water purification and metal ions removal at very low concentrations in chemical processes industries (Alexandratos and David 1986).

Global world production of plastics rose from 204 M tons in 2002 to 288 M tons in 2012 (about 41%) (Europe, Plastic 2013). Polystyrene (PS), is one of the six most common types of plastics, forms 7.3% of this production (Uluturk et al, 2013). It is a cheap and hard plastic and is manufactured by vinyl polymerization of styrene free radical. A large portion of PS is used in production and protective packaging (clamshells, cups, plates, trays, bowls, cottage cheese containers and yogurt). There are some methods for recycling polystyrene waste, including chemical and thermal recycling. The waste plastic (WP) is formed from many types: polystyrene, polyethylene, polypropylene, and others. Moreover, the form of these materials is extremely varied; it includes films, bags, plastic bottles, and Styrofoam (Chaupt et al, 1998).

WP can be generally modified or treated depending on the chemical structure of the backbone chain. In order to obtain valuable raw materials from polyesters or polyamides, they should be treated chemically, which could be used for different applications (Jacques et al, 2002; Tabekh et al, 2012 and Tabeikh et al, 2013). WP resins are characterized by: long life, low cost, low maintenance, easy to handle, easy to recover and reuse, etc. (APHA, 1960).

Yasuhito and Shigeo (2001) succeeded in converting waste polystyrene from electrical appliances into a polymer flocculent for treating some kinds of waste after chemical modification. Bekri et al, (2008), Mohamed (2016), Ehssan et al. (2018) studied the possibility of using waste polystyrene to remove water hardness.

Sivasubramanian et al. (2012) deal with the application of algal technology (Phytoremediation) to reduce total hardness in waste waters and industrial effluents.

In this respect, the present study focuses on water management through using low cost and waste materials through recycling waste polystyrene into modifying sulfonated waste polystyrene by using marine algae (*Ulva fasciata*) embedded in SWPS. This treatment method can reduce effectively the water hardness, Mg or Ca hardness besides sulfate and phosphate from very hard water. This work also aims to carry out performance evaluation studies at different parameters namely; flow rates, resin dosages, pH and temperature variations for sulfonated waste polystyrene (SWPS) resin and modified sulfonated waste polystyrene (MSWPS) resin to determine the optimum removal efficiency.

## II. MATERIALS AND METHODS

### 2.1. Preparation of WPS Resin

White coffee cups and the food packing were crushed till particles size (0.2 - 0.3) cm<sup>3</sup>. The method used for resin preparation was according to Bekri (Bekri-Abbes et al, 2008). Five grams of dry material (WPS) and 100 mL of 95% H<sub>2</sub>SO<sub>4</sub> acid were poured in a flask and left under agitation to react while temperature and time are varied. Finally, the in used sulfuric acid was decanted and the beads (SWPS) were washed with deionized water (6-7 times) and dried at 60°C for 2h. Then the beads (SWPS) reacted with 1M NaCl solution for 2h to be neutralized and convert H<sup>+</sup> to Na<sup>+</sup>. The degree of beads sulfonation (SWPS) was estimated by titration through dissolving 0.3 g of SWPS in about 30 mL of a toluene/ methanol mixture (90/10 v/v) (Bekri-Abbes et al, 2008). The solution of SWPS was titrated against 0.02M NaOH dissolved in methanol with phenolphthalein as indicator. The degree of sulfonation was found (17%) using this equation:

$$\text{Degree of sulfonation} = [N.V / ((w-81.N.V)/104)].100$$

Where: N; normality in (mole/L) and V; volume in (liters) of sodium hydroxide methanol solution, w is the weight in (g) of sulfonated polystyrene sample, 104 and 81 are the molar mass of the styrene unit and -SO<sub>3</sub>H groups; respectively.

### 2.2. Collection and preparation of the marine Algae in Nano-Scale

*Ulva fasciata* algae were collected from the Egyptian Mediterranean Sea coast in front of Alexandria. The algae were washed with fresh water followed by distilled water in order to remove the salts, then dried for 5 days at a shady place, followed by drying for 2 h in an oven at 70 °C and milling to a powdery form. Five grams of the powder was sonicated in 100 mL double distilled water for 2 h, then micro filtered at mesh size (0.22µm) to remove large particles.

A simple sonication method was used to prepare the Nano-extracts (Darvishi and Morsali 2010 and Masoudzadeh et al, 2019) where the produced filtrate was sonicated by (ultrasonic generator model: CREST ULTRASONICS) for 5 hours, then centrifuged at 8,000 rpm for 15 minutes. By this centrifugation, it was seen that

the extract was purified from a significant amount of supernatants. The supernatant was collected and diluted with a small amount of double distilled water to detect the size of its particles by the Zetasizer Nano Instrument (model: Malvern ZEN5600). The concentration of the stock solution was determined using freeze-drying (model: Labconco 3). The SWPS was immersed directly in the supernatant nanoparticle aqueous solution extract (100 mg/L) without shaking for 2 h to obtain the modified resin MSWPS.

### 2.3. Hard water preparation

Different types of hard water have been prepared: most chemicals were obtained from Sigma Aldrich and used without further purification unless specified.

#### 2.3.1. The first hard water preparation used in (SWPS) resin

Calcium and magnesium salt solutions of concentrations of 30, 50, 100, 150 and 200 mg/L were prepared by diluting the initial calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) stock solutions (prepared from CaCl<sub>2</sub> or MgCl<sub>2</sub> respectively) in a liter of DW. Very hard water was prepared by dissolving 1 g of Ca Cl<sub>2</sub> and 1g of MgCl<sub>2</sub> in a liter of DW. The initial and final Ca<sup>2+</sup> and Mg<sup>2+</sup> ion concentrations analysis were performed using the EDTA method (Grasshoff 1999 and Cash, 2008).

#### 2.3.2. The second hard water preparation used in (MSWPS) resin

Calcium chloride, magnesium chloride, Sodium sulfate and sodium hydrogen phosphate were obtained from Merck in analytical grade. To detect the removal efficiency of MSWPS resin; four hard water samples were prepared using deionized water (DW) were summarized in Table (1).

**Table 1: Samples preparations of different concentrations of hard water and some inorganic pollutants in a liter of DW.**

Parameter	1 <sup>st</sup> conc.	2 <sup>nd</sup> conc.	3 <sup>rd</sup> conc.	4 <sup>th</sup> conc.
Ca mg/l	100	150	200	250
Mg mg/l	100	150	200	250
PO <sub>4</sub> <sup>3-</sup> mg/l	95	190	285	380
SO <sub>4</sub> <sup>2-</sup> g/l	1	1.5	2	2.5

The concentration of phosphate or sulfate was analyzed according to the methods described by Grasshoff (1999) and Bather and Riley (1954). The total hardness (T.H) analysis was measured using the EDTA titrimetric method and calculated according to the equation of water hardness (Cash, 2008), where:

Water total hardness (T.H); mg/L as CaCO<sub>3</sub> = 2.497 [Ca; mg/L] + 4.118 [Mg; mg/L].

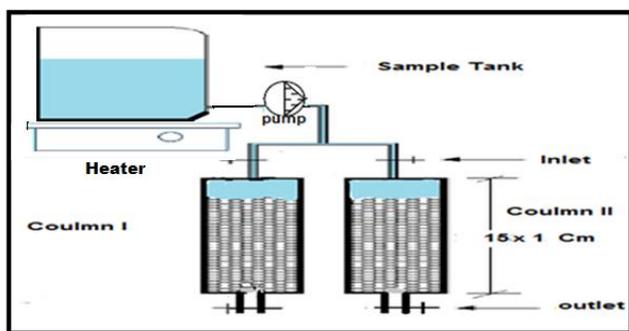
The percentage removal of hardness was calculated using the following relationships (Srivastava et al, 2008):

$$\% \text{ Removal} = C_i - C_f / C_i \times 100$$

Where, C<sub>i</sub> and C<sub>f</sub> are the initial and final hardness in mg/L respectively.

#### 2.4. *Experimental Setup*

The experimental setup consisted of two columns of a height of 15 cm and a diameter of 2 cm in which sulphonated waste polystyrene (SWPS) and modified sulphonated waste polystyrene (MSWPS) were performed (Fig. 1). The column is closed with end caps at both ends as in Fig. 1. The mesh was made at bottom in order to avoid any column flow. SWPS beads of 5-6 mm in diameter were used as packed media to study elution efficiency. Hard water (HW) sample (1L) was pumped in the column with a flow rate of  $(100 - 400) \pm 5$  mL/min,  $\text{pH} = 4.5 - 11.5 \pm 0.3$ ,  $T = 20 - 35^\circ\text{C} \pm 5^\circ\text{C}$  and resin dose of  $1 - 5.0 \pm 0.1$  g to find out the optimum condition for each test. For SWPS, the HW samples were analyzed for  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and T.H, while for MSWPS the HW samples were analyzed for  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ , T.H,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  to determine the removal efficiency.



**Fig. 1: Schematic of Experimental Setup for column studies**

#### 2.5. *Characterization of Resin*

The FTIR spectra for the KBr discs of the WPS, SWPS and MSWPS were recorded using a Bruker Vertex 70 spectrophotometer with a spectral domain  $400 - 4000$ ,  $4 \text{ cm}^{-1}$  resolution. Surface morphology analysis of adsorbents before and after modification was characterized by the SEM technique using QUANTA and FEG250.

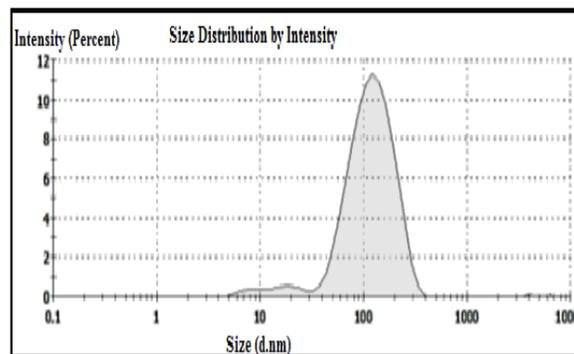
### III. RESULTS AND DISCUSSION

#### 3.1. *Characterization the average particles size of Nano natural extracts of (Ulva fasciata) algae*

The image in Fig. 3 (c) demonstrated uniform dispersion of nanoparticles throughout the SWPS, with no evidence of aggregation, which was only visible in this MSWPS image. These results demonstrate that the SWPS surface alteration was influenced by the modification process. As a result, the MSWPS had a large surface area, which improved the efficacy of hardness removal by increasing the area of adsorbents on the resin surface.

Using the ultrasonic radiation method in the preparation of nanomaterials is a low-cost, high-efficiency technology that does not require high temperatures or pressure. In addition, it can be applied widely in industrial applications due to its low cost and environmentally friendly nature (Zhan et al, 1999).

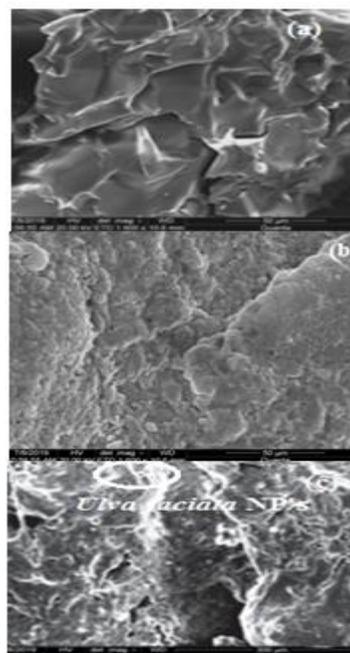
Furthermore, the average particle size of the nano-extract of *Ulva fasciata* algae is 86.78 nm according to this study's dynamic light scattering analysis (Fig. 2).



**Fig. 2: The average size of *Ulva fasciata* algae particles in water extract**

#### 3.2. *SEM Analysis*

The surface morphology of the WPS, SWPS and MSWPS was examined by using a scanning electron microscope as shown in Fig. 3 (a, b, c). The (WPS) has a highly smooth and shiny surface with almost no holes. The SWPS surface was porous with many voids and holes due to the sulfonation of WPS. The surface of SWPS was still smooth despite the presence of a few large blocks. The surface appeared to be rougher, fractured with random small pores after treatment with nano extract of marine algae (*Ulva fasciata*), as illustrated in Fig. 3.



**Fig. 3: SEM of: (a) (WPS); (b) (SWPS); (c) MSWPS)**

The image in Fig. 3 (c) demonstrated uniform dispersion of nanoparticles throughout the SWPS, with no evidence



the ion exchanger surface. Anh et al, (2020) obtained the same findings that when the flow rate decreased, the initial concentration, and the mass of sulfonated polystyrene increased, the adsorption capacity was observed to increase through their study by investigating the feasibility of sulfonating polystyrene waste by using sulfuric acid to form sulfonated functional groups on the polystyrene matrix then used for heavy metal removal from wastewater.

### 3.4.1.2. The effect of resin dosage (g)

The removal amounts are shown in Fig. 6. The removal amount of calcium, magnesium and total hardness from synthetic hard water prepared in triplicate was investigated in relation to the resin dose that was between 1 and 5g under experimental conditions when  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  concentrations were at 150 mg/L,  $T = 25^\circ \pm 0.5^\circ\text{C}$  and pH of the solution was adjusted at  $(7.5 \pm 0.3)$ . The removal efficiency of calcium, magnesium, and total hardness increases as the amount of resin is increased, as shown in Fig. 6 (b). The amount of resin used is a crucial factor in determining the calcium and magnesium ions quantitative uptake as well as total hardness. This could be explained by the fact that when the resin amount increases, it causes a great ion exchange sites to replace earth alkaline metals of a fixed initial concentration of calcium and magnesium in the solution of hard water and total hardness (Mahmoud et al, 2015).

The effect of various doses of resin from 1 g to 5 g was studied. From Fig. 6 (b), it was found that with an increase in resin dosage from 1 to 5 g, the removal capacity increased due to the active site increase on the surfaces of the resin, as discussed by Mahmoud et al, (2016).

### 3.4.1.3. The effect of varying temperature ( $^\circ\text{C}$ )

The removal percentage of Ca, Mg ions and total hardness samples at different temperatures are shown in Fig. 6 (c). The maximum removal capacity of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and total hardness obtained from samples were found at  $\text{pH} = 11.5 \pm 0.5$ , flow rate =  $100 \pm 10$  ml/min, resin dose =  $5.0 \pm 0.1$  g, Ca, Mg and total hardness concentrations were 150 mg/L, 150 mg/L and 540 mg  $\text{CaCO}_3$  /L; respectively. As the temperature of the reaction increased from  $20^\circ\text{C}$  to  $35^\circ\text{C}$ , the removal capacity for calcium ions, magnesium ions, as well as total hardness increased (Fig. 6 (c)). As the temperature rises, the energy levels of the molecules participating in the reaction rise, increasing the rate of the reaction. According to Mohammad et al, 2013, this shows that the process is endothermic.

### 3.4.1.4. The effect of pH

The variation in hydrogen ion concentration affects the number of metal ions binding sites on the adsorbent surface. The initial pH of the hard water solution was controlled with a pH meter by adding hydrochloric acid or sodium hydroxide solutions. The temperature, the flow rate and resin dosage were kept constant in this experiment at  $25 \pm 0.5^\circ\text{C}$ ,  $100 \pm 10$  ml/min for 1L and  $5.0 \pm 0.1$ g. The

effect of different pH values (4.5, 7.5, and 11.5) on the removal of calcium and magnesium ions from synthetic hard water solution and total hardness is shown in Fig. 6 (d). Because there is an abundance of hydrogen ions in solution, the values of the metal ions adsorption capacity rise with increasing the solution pH, as the adsorption of magnesium ions and total hardness values are higher in basic media than in acidic media (Maicaneanu et al, 2014).

For various concentrations of total hardness, it is evident that as the concentration of the solution increases, total hardness removal decreases, with the best removal observed in the basic medium (Fig. 6 (d)).

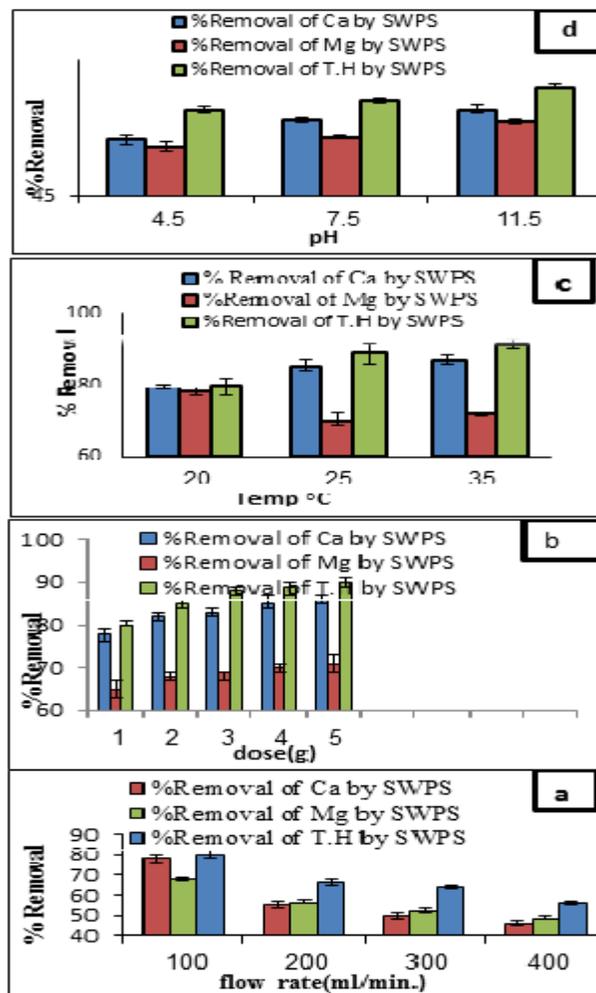


Fig. 6: Effect of varying: (a) flow rate, (b) resin dosage, (c) temperature and (d) pH on the ability to remove Ca, Mg ions and T.H for SWPS

Finally, it can be seen from Fig. 6 (a, b, c, d) that the optimum condition for removal capacity of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and T.H was at a dose  $5.0 \pm 0.1$ g, flow rate of 100 mL/min for 1L, a temperature of  $35 \pm 0.5^\circ\text{C}$  and a pH of  $11.5 \pm 0.3$ .

### 3.4.2. An application on using (SWPS) for the removal hardness in natural water conditions

Given that changing the pH and the temperature of the hard water to be treated will raise the treatment cost, therefore it was decided in this research to change the optimum state for the treatment of water hardness under natural water conditions to be; temperature = 25°C and pH = 7.5 as shown in Fig. 7 (a, b). For the preparation of hard water, the concentrations of calcium, magnesium ions and T.H were (30, 50, 100, 150, 200) mg/L of Ca<sup>2+</sup> or Mg<sup>2+</sup> and (198, 330, 661, 992, 1323 CaCO<sub>3</sub> mg/l) for T.H, respectively. The ability to remove Ca, Mg and T.H using SWPS varies from 200 to 68 mg/L for Ca ions, from 200 to 77 mg/l for Mg ions and from 1323 to 251mgCaCO<sub>3</sub>/L for total hardness. The behavior of SWPS resin for calcium and magnesium ions sorption in solution is shown in Fig. 7 (a, b). SWPS select calcium more than magnesium, and its exchange capacity for calcium is larger.

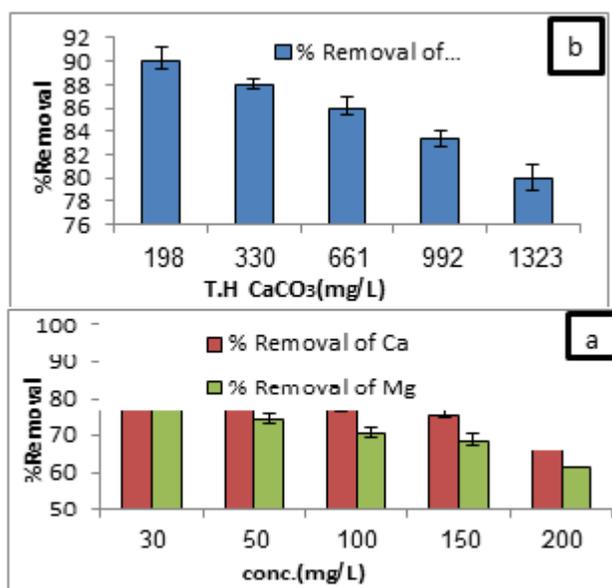


Fig. 7: Ability of removal of ions: (a) calcium, magnesium ions and (b) TH for SWPS at natural water conditions.

**3.4.3. Column II (MSWPS) applications for hardness and Some Inorganic Pollutants water samples**

Column II (MSWPS) resin studies the removal of Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> ions and T.H from synthetic hard water samples at a dose of 5.0 ± 0.1g, flow rate 100 mL/min, temperature of 25 ± 0.5°C and pH 7.5±0.3. Parameter concentrations and the removal % were measured at triple times. Table (2) shows that the MSWPS resin which had nano extract of marine algae (*Ulva fasciata*) improved the removal efficiency for Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and Total Hardness. The same results were obtained by Tadros et al, (2019). The increased surface area of the cation exchange resulted in an improvement in the hardness treatment performance, which improved the removal efficiency of the investigated parameters.

**Table 2: Removal efficiency for Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and T.H using MSWPS**

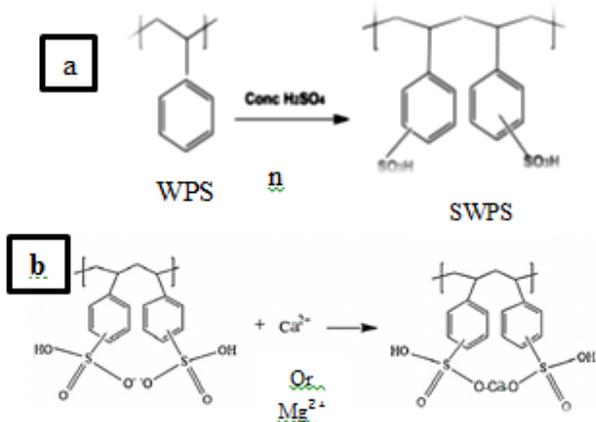
Parameter	Conc. before treatment	St. Dv ±.	Conc. after treatment	St. D v±.	% Removal	St. D v±
Ca <sup>2+</sup> (mg/L)	100	0.58	5.6	0.05	94.40	0.35
	150	0.45	13	0.08	91.33	0.38
	200	0.30	23	0.16	88.50	0.32
	250	0.15	45	0.05	82.00	0.30
Mg <sup>2+</sup> (mg/L)	100	0.56	13	0.06	87.00	0.21
	150	0.50	26	0.05	82.66	0.20
	200	0.3±6	39	0.24	80.50	0.40
	250	0.21	67	0.07	73.20	0.25
PO <sub>4</sub> <sup>3-</sup> (mg/L)	50	0.12	5.60	0.09	88.80	0.31
	95	0.20	16	0.29	83.16	0.82
	150	0.35	34	0.24	77.33	0.47
	200	0.10	89	0.52	55.50	0.25
SO <sub>4</sub> <sup>2-</sup> (g/L)	0.50	0.02	0.13	0.02	74.00	0.27
	1.00	0.01	0.36	0.01	64.00	0.20
	1.50	0.02	0.71	0.01	52.67	0.36
	2.00	0.01	1.05	0.02	47.50	0.10
TH (mgCaCO <sub>3</sub> /L)	660	0.23	60.4	0.36	90.85	0.61
	992	0.17	113	0.55	88.60	0.29
	1323	0.12	198.5	0.26	85.00	0.52
	1654	0.05	365	0.52	78.00	0.55

After adding nano marine algae extract (*Ulva fasciata*) to the (SWPS), the removal efficiency increased for prepared water hardness (1323 mgCaCO<sub>3</sub>/L), Ca<sup>2+</sup>, Mg<sup>2+</sup> ions (200mg/l) from (80% to 85%), (66% to 88.5%) and (61.6 to 80.5%) respectively; beside removal of SO<sub>4</sub><sup>2-</sup> (1.5 g/l) up to 52.7%, and PO<sub>4</sub><sup>3-</sup> (150 mg/l) up to 77.3%.. The marine environment is incomparable reservoirs of

bioactive so this new function groups which is absorbed on MSWPS is a result of the addition of a nano marine algae extract (*Ulva fasciata*) as described by Zbakh et al., (2012).

### 3.5. The mechanism of water hardness removal

The mechanism of the ion exchange reaction is as follows:



The SWPS cationic resin has a cross linked polystyrene with divinylbenzene and contains sulfonic type functional groups. The Ca (II) retention from the samples that were used in the experiment in contact with the resin occurs through mechanisms that do not involve new chemical reactions, but only ion exchange reactions with the participation of the functional groups, which result in a rearrangement of the surrounding water molecules as a result of the ion exchange process. The FTIR peaks associated with chemical bonding in this type of material are well-known (Dean, 1995; Bekri-Abbes et al, 2008; Singare et al, 2011) and the same observations were made by (Liliana et al, (2014).

A schematic diagram shows that the surface area of SWPS resin is bigger than that of WPS and sodium ions on its surface could be substituted easily by calcium or magnesium ions. The MSWPS showed the biggest surface area, allowing for greater Na<sup>+</sup> ion replacement by Ca<sup>2+</sup> or Mg<sup>2+</sup> ions (Fig. 8).

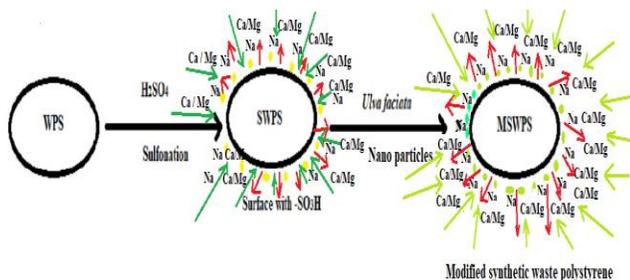


Fig. 8: The mechanism of hardness removal using MSWPS

## IV. CONCLUSIONS

- Sulfonation and the addition of a nano extract of marine algae (*Ulva fasciata*) improved the WPS in this study, which will be applied to investigate the capability of sulfonated or modified recycled polymers made from waste products.
- The optimum conditions for the removal of Ca<sup>2+</sup>, Mg<sup>2+</sup> and T.H. concentrations by using (SWPS) or (MSWPS) were found to be at temp. = 35°C, flow rate = 100 mL/min, pH = 11.5 and resin dose = 5.0g.
- The SWPS was efficient in reducing Ca<sup>2+</sup>, Mg<sup>2+</sup> ions and T.H concentrations to below the permitted limits, which is necessary to meet drinking water quality standards at temp. = 25°C, flow rate = 100 mL/min, pH = 7.5 and resin dose = 5.0g.
- The greatest removal effectiveness for calcium, magnesium, and T.H was 80 percent, 75 percent, and 89 percent, respectively, for various samples treated with SWPS under optimal circumstances.
- After adding nano marine algae extract (*Ulva fasciata*) to the (SWPS), The removal efficiency of prepared water hardness increased from 80% to 85%,66% to 88% ,61.6 to 80.5% for T.H.Ca and Mg respectively; beside removal of SO<sub>4</sub><sup>2-</sup> (1.5 g/l) up to 52.7%, and PO<sub>4</sub><sup>3-</sup> (150 mg/l) up to 77.3%.
- The surface of SWPS treated with nano marine algae extract (*Ulva fasciata*) appeared to be rougher and contained smaller random pores, indicating that the MSWPS had a large surface area to increase the contact between the ions and the resin, improving the efficiency of hardness removal.

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## REFERENCES

- [1] Alexandratos, S. and David, L. (1986). "Dual-mechanism bifunctional polymers: polystyrene-based ion-exchange/redox resins". *Macromolecules* 19 (2): 280-287. <https://doi.org/10.1021/ma00156a006>
  - [2] American Public Health Association (1960). *Standard methods for the examination of water and wastewater* (11th ed.) Prepared and published jointly by American Public Health Association, American Water Works Association, and Water Pollution Control Federation. New York, N. Y.: APHA (1790 Broadway), 1960. 626 pp.
- New York, N. Y.: APHA (1790 Broadway), 1960. 626 pp. Anh, T.K.T., Thim Th.Ph., Quoc, H.N., Nhung, T.T.H., Duy, T.B., Minh, T.N., Manh, Kh.N., Bart, V.d.B. (2020). From waste disposal to valuable material: Sulfonating polystyrene waste for heavy metal removal. *Journal of Environmental Chemical Engineering*, 8(5) October 2020, 104302. <https://doi.org/10.1016/j.jece.2020.104302>
- Arockia sahayaraj, P.; Gowri, J.; Dharmalingam, V.; Shobana, R. and PremaInt, A. ( 15)

- [3] [3] Anh, T.K.T., Thim Th.Ph., Quoc, H.N., Nhung, T.T.H., Duy, T.B., Minh, T.N., Manh, Kh.N., Bart, V.d.B. (2020). From waste disposal to valuable material: Sulfonating polystyrene waste for heavy metal removal. *Journal of Environmental Chemical Engineering*, 8(5) October 2020, 104302. <https://doi.org/10.1016/j.jece.2020.104302>
- [4] [4] Arockia sahayaraj, P.; Gowri, J.; Dharmalingam, V.; Shobana, R. and Premalnt, A. (2015). "Phytochemical screening by FTIR spectroscopic analysis of leaf and stem extracts of wedelia biflora". *J Nano Corr. Sci. and Eng.* 2(5): 322-334. <http://www.ijnscse.com> ISSN Online: 2395-701
- [5] [5] Bather, J. and Riley, J. (1954). "The chemistry of the Irish Sea Part I. The Sulphate-Chlorinity Ratio" *ICES Journal of Marine Science* 20 (2): 145-152. <https://doi.org/10.1093/icesjms/20.2.145>
- [6] [6] Bekri-Abbes, I., Bayouhd, S., Baklouti, M. (2008). "The removal of hardness of water using sulfonated waste plastic." *Desalination* 222(1-3): 81-86. <https://doi.org/10.1016/j.desal.2007.01.121>
- [7] [7] Bekri-Abbes, I.; Bayouhd, S. and Baklouti, M. (2006). "Converting waste polystyrene into adsorbent: potential use in the removal of lead and cadmium ions from aqueous solution". *Journal of Environmental Polymer Degradation* 14: 249-256. DOI 10.1007/s10924-006-0018-3
- [8] [8] Cash, D. (2008). "EDTA titrations 2: Analysis of calcium in a supplement tablet; Analysis of magnesium in Epsom salt; hardness of water." *Chemical, Environmental, and Biotechnology Department, Mohawk College of Applied Arts and Technology*: pp. 20. Available at: <http://www.uclmail.net/users/dn.cash/EDTA2.pdf>.
- [9] [9] Chaupart, N., Serpe, G. and Verdu, J. (1998). "Molecular weight distribution and mass changes during polyamide hydrolysis" *Polymer* 39 (6-7): 1375-1380. [https://doi.org/10.1016/S0032-3861\(97\)00414-X](https://doi.org/10.1016/S0032-3861(97)00414-X)
- [10] [10] Darvishi, Z. and Morsali, A. (2010). "Synthesis and characterization of Nano-bentonite by sonochemical method". *Ultrasonics sonochemistry* 18 (1): 238-242. DOI: 10.1016/j.ulsonch.2010.05.012 PMID: 20579927
- [11] [11] Dean J.A., (1995). *Dean's Analytical Chemistry Handbook* second edition (McGraw-Hill Handbooks) is written by Pradyot Patnaik and published by McGraw-Hill Inc., New York.
- [12] [12] Europe, Plastic. "Plastics-The Facts (2013): An analysis of European latest plastics production, demand and waste data." *Plastic Europe* 1 (2013): 40.
- [13] [13] Grasshoff, K.; Kremling, K. and Ehrhardt, M. (1999). "Methods of Seawater Analysis" 3ed, Completely Revised and Extended Edition, Wiley-VCH. Weinheim. New York. Chichester. Brisbane. Singapore. Toronto. Printed in the Federal Republic of Germany. 634 p. ISBN 3-527-29589-5
- [14] [14] Gray, N. (2010). "Water Technology: An Introduction for Environmental Scientists and Engineers,". 3rd Edition, pp: 403-459.
- [15] [15] Hussein, P.D.M., Nassef, P.A.D.E., Ibrahim, E.M.A. (2016). "Water Hardness Removal by Using Waste Polystyrene." *DRP JOURNAL OF POLYMER SCIENCE & TECHNOLOGY* 1(1): 1-5. <http://www.dx.doi.org/10.25177/JNMS.2.1.1>
- [16] [16] Inagaki, Y., Kiuchi, S. (2001). "Converting waste polystyrene into a polymer flocculant for wastewater treatment." *Journal of Material Cycles and Waste Management* 3(1): 14-19. <https://doi.org/10.1007/s10163-000-0033-8>
- [17] [17] Jacques, B.; Werth, M.; Merdas, I. and Thominette, F. (2002). "Hydrolytic ageing of polyamide 11. 1. Hydrolysis kinetics in water". *Polymer* 43 (24): 6439-6447. DOI: 10.1016/S0032-3861(02)00583-9
- [18] [18] Klemes, J., Robin, S., and Jin-Kuk, K. (2008). *Handbook of water and energy management in food processing*. Elsevier, 1506 p. ISBN 9781845691950, 9781845694678.
- [19] [19] Liliana, L., Bogdan, B., Ramona-Elena, T-F., Mioara, D., Laura, Gheorghe, G. (2014). FTIR analysis of ion exchange resins with application in permanent hard water softening. *Environmental Engineering and Management Journal* (2014), 13(9): 2145- 2152. DOI:10.30638/EEMJ.2014.237
- [20] [20] Mahmoud, F.; Abdel Moghny, Th.; Awad Allah, A.; Abdou, M. and Abdel Hameed, A. (2015). "Kinetic Study of Ca (II) and Mg (II) on High Crosslinked PS-DVB Synthetic Resin from Chromium Solution". *International Journal of Modern Organic Chemistry* 4 (1): 40-55. [www.M.S.P.com/Journals/IJOrgChem.aspx](http://www.M.S.P.com/Journals/IJOrgChem.aspx) ISSN: 2166-0174
- [21] [21] Mahmoud, M.; Abdou, A. and Ahmed, S. (2016). "Conversion of waste styrofoam into engineered adsorbents for efficient removal of cadmium, lead and mercury from water". *ACS Sustainable Chemistry & Engineering* 4 (3): 819-827. <https://doi.org/10.1021/acssuschemeng.5b01149>
- [22] [22] Maicaneanu, A.; Varodi, C.; Bedeleian, H. and Gligor, D. (2014). "Physical-chemical and electrochemical characterization of Fe-exchanged natural zeolite applied for obtaining of hydrogen peroxide amperometric sensors". *Geochemistry* 74 (4): 653-660. <https://doi.org/10.1016/j.chemer.2014.02.005>
- [23] [23] Martins, C.; Ruggeri, G. and De Paoli, M. (2003). "Synthesis in pilot plant scale and physical properties of sulfonated polystyrene". *Journal of the Brazilian Chemical Society* 14 (5): 797-802. <http://dx.doi.org/10.1590/S0103-50532003000500015>
- [24] [24] Masoudzadeh, F., Masoud, J. and Mohammad, F. (2019). "Preparation and application of cellulose nano whiskers (CNWs) in engineered cementitious composites". *Journal of Building Engineering* 21: 213-221. <https://doi.org/10.1016/j.jobe.2018.10.020>
- [25] [25] Mohammad, S., Mansur, Z., Hossein, K., Abdeltif, A., Kamiar, Y., (2013). Removal of hardness agents, calcium and magnesium, by natural and alkaline modified pumice stones in single and binary systems. *Applied Surface Science*, 274: 295-305. <https://doi.org/10.1016/j.apsusc.2013.03.042> ff10.1016/j.apsusc.2013.03.042ff. ffhal-00915133f <https://hal.archives-ouvertes.fr/hal-00915133>
- [26] [26] Nassef, E., Mousa, M., Elgayar, D.A., Hussein, M. (2018). "A Novel Technique for Water Hardness Removal by Using Polystyrene." *Australian Journal of Basic and Applied Sciences* 12(7): 126-138. DOI:10.22587/ajbas.2018.12.7.20 Corpus ID: 195322431
- [27] [27] Negm, M.; Ibrahim, H.A.H.; Shaltout, N.A. and Hamdona, S.K. (2018). Green Synthesis of Silver nanoparticles Using Marine Algae Extract and Their Antibacterial Activity, *Middle East Journal of Applied Sciences*, 13 (1)957-970. ISSN 2077-4613
- [28] [28] Pentamwa, P., Wipasinun, Th. and Suparat, N. (2011). "Hardness Removal from Groundwater by Synthetic Resin from Waste Plastics". *Proceedings of 2011 4th International Conference on Environmental and Computer Science (ICECS 2011)*.
- [29] [29] Radhika, D. and Mohaideen, A. (2015). "Fourier transform infrared analysis of ulva lactuca and gracilaria corticata and their effect on antibacterial activity". *Asian J. Pharm. Clin. Res.*, 8(2): 209-212. ISSN-0974-2441
- [30] [30] Schaep, J.; Van der Bruggen, B.; Uytterhoeven, S.; Croux, R.; Vandecasteele, C.; Wilms, D.; Van Houtte, Emmanuel and Vanlerberghe, F. (1998). "Removal of hardness from groundwater by nano filtration". *Desalination* 119 (1-3): 295-301. [https://doi.org/10.1016/S0011-9164\(98\)00172-6](https://doi.org/10.1016/S0011-9164(98)00172-6)
- [31] [31] Singare P.U., Lokhande R.S., Madyal R.S., (2011). Thermal degradation studies of some strongly acidic cation exchange resins, *Open Journal of Physical Chemistry*, 1: 45-54. 2152 <http://omicron.ch.tuiasi.ro/EEMJ/>
- [32] [32] Sivasubramanian, V., Subramanian, Muthukumar, M., Murali, R., Vivekananda, R. (2012). "Algal technology for effective reduction of total hardness in wastewater and industrial effluents." *Phykos* 42(1): 51-58. Corpus ID: 110137272
- [33] [33] Srivastava, V.; Mall, I. and Mishra, I. (2008). "Adsorption of toxic metal ions onto activated carbon: Study of sorption behaviour through characterization and kinetics". *Chemical Engineering and Processing: Process Intensification* 47 (8): 1269-1280. <https://doi.org/10.1016/j.ccep.2007.04.006>
- [34] [34] Tabeikh, H., Al Kurdi, M.H. and Ajji, Z. (2013). "Effect of Metal Ions on the Chemical Recycling of Poly (Ethylene Terephthalate) in Sulphuric Acid." *Revue Roumaine de Chimie* 58 (11-12): 887-890. <http://web.icf.ro/rch/>
- [35] [35] Tabeikh, H.; Al Kurdi, M.H. and Ajji, Z. (2013). "Effect of Cd<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Al<sup>3+</sup>, Co<sup>2+</sup> ions on the chemical recycling of

poly (ethylene terephthalate) in sulphuric acid." Polimeri: časopis za plastiku i gumu 34 (4): 97-100. UDK 678.74:66.094.941

- [36] [36] Tabekh, H., Koudsi, Y. and Aji, Z. (2012). "Chemical recycling of poly (ethylene terephthalate) using sulfuric acid". Rev. Roum. Chim 57 (12): 1029-1034. <http://web.icf.ro/rch/>
- [37] [37] Tadros, H.; Hamdona, S.; Ghobrial, M.; El-Naggar, M. and Abd El-Hamid, O. (2019). Wastewater treatment of Mariout Lake drains using combined physical chemical and biological methods in microcosm experiments". Aquatic Science and Technology, 7 (2): 46-70. ISSN 2168-9148. <http://dx.doi.org/10.5296/ast.v7i2.14651>
- [38] [38] Uluturk, I., Kim, Y. and Yang, C. (2013). "Developing ion exchange membrane from waste expanded polystyrene for heavy metal removal from industrial wastewater" University of Massachusetts Dartmouth, USA, AFS 2013 Spring Conference, 2013.
- [39] [39] Zhan, H.; Yang, X.; Wang, D.; Xie, Y. and Qian, Y. (1999). "Synthesis of nanocrystalline PbSe by sonolysis of Pb(NO<sub>3</sub>)<sub>2</sub> in non-aqueous solvent". Inorg. Chem. Commun. 2(10): 447-249. [https://doi.org/10.1016/S1387-7003\(99\)00118-5](https://doi.org/10.1016/S1387-7003(99)00118-5)

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