Efficiency of Synthetic Resin Amberjet-4200 and Dowex-50 in the Removal of Divalent Ions Mg (II), Mn (II), Zn (II) and Pb (II) Ions from Wastewater

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Abstract
The aim of the current research is to study the feasibility and the efficiency of synthetic Resin Amberjet-4200 and Dowex-50 in the removal of divalent ions Mg (II), Mn (II), Zn (II) and Pb (II) ions from wastewater. The research consisted of three phases; a preliminary comparative study, batch equilibrium tests and fixed-bed column tests. The main considered points from the three phases of the research are summarized as follows:
* It has been noted that the removal efficiency of Mg (II), Mn (II), Zn (II) and Pb (II) ions by the synthetic resins of Dowex-50 and Amberjet-4200 in phase I of the research, these synthetic resin has yielded the highest removal of 83.5%, at a dose of 3g/l and pH 5.4.
* Treatment using acid has increased the removal efficiency of from 83.5% to 94.50%, which was the highest percent removal achieved among all the studied resins.
* Treatment using alkaline as KOH prior to tartaric acid treatment did not prove any enhancement in the removal of Mg (II), Mn (II), Zn (II) and Pb (II) ions, as TA-N-SB has only yielded 66.14% uptake, compared to 88.50% by these resins. Therefore, a OH treatment is considered a dispensable step in the treatment process.
* Each of them or the separate one of Dowex-50 achieved very high removal efficiency; however, their high alkalinity would limit their industrial applications.
* Amberjet-4200 is considered the most promising sorbent for the uptake of Mg (II), Mn (II), Zn (II) and Pb (II) due to its high efficiency, economic feasibility, and simplicity of preparation.


1. Introduction
The use of solutions with variable saline concentrations for man is indispensable for the industrial and physiologic activities, especially in clinical Chemistry. Solutions of NaCl 0.9% m/v are used as physiologic solution; because it reflects the isotonic composition of the biologic’s fluids of the human body. The determination of metals in this sample is very important because contamination of sodium salts and water can complicate the conditions of the patients that use dialysis solutions.

The determination of Mg (II), Mn (II), Zn (II) and Pb (II) in natural waters is also important whereas these trace elements present in the matrix constitute an environmental problem and there is a lack of information on the behavior and toxic potential of these metals on the metabolism of living organisms.

Oxygen and electrons transport, constituent of enzymes to redox reactions and involvement in the mobilization of iron to hemoglobin synthesis. Zinc, essential trace element for man, has been reported since 1934. It is as associate in the insulin production, in the composition of more 90 enzymes related with acid-base catalysis, and in DNA and RNA synthesis. The manganese is associated with cartilages and bones formation.

Inductively coupled plasma is nowadays considered as the most sophisticated and common method for trace metal determination in various materials. Thus, trace determination in saline solutions always needs a prior separation and pre-concentration steps. Several procedures extensively used for separation and pre-concentration include liquid-liquid extraction and solid phase extraction. However, solvent extraction suffers with problems for handling of large sample volume, mutual solubility of two phases, and emulsion formation. Consequently, in the last decade use of chelating resins for metal enrichment has increased very significantly.

Their advantages include good selectivity, higher-concentration factor, easy regeneration for multiple sorption-desorption cycles and good reproducibility in the sorption characteristics. Alizarin Red S (sodium1, 2-dihydroxy-anthraquinone-3-sulfonate, ARS) reacts with various metal ions to form anionic chelates, which are not extractable into organic solvents. ARS was studied for separation and pre-concentration of Mg (II), Mn (II), Zn (II) and Pb (II) in different matrices, such as alloys, biological samples and environmental samples. Therefore, the potential use of ARS impregnated in resins has been scarcely explored for analytical procedures employing separation and pre-concentration.

The aim of this work was to explore the possibility of the application of a chelating resins obtained by immobilization the reagent alizarin red S (ARS) on nonionic polymer sorbent Amberjet-4200 and anion exchanger Dowex-50 for Mg (II), Mn (II), Zn (II) and Pb (II) separation and pre-concentration from saline samples. The sorbet elements are...
subsequently eluted with nitric acid and determined using ICP spectrometry. The conditions have been optimized and the methods applied for the determination of Mg (II), Mn (II), Zn (II) and Pb (II) in physiological solutions and seawater samples.

2. Experimental:

2.1. Reagents

All reagents were of analytical reagent grade. Double distilled and deionizer waters were used for the preparation of solutions. The laboratory glassware was kept overnight in a 10% v/v nitric acid solution. Before use, the glassware was washed with deionizer water and dried in a dust-free environment. Metal stock solutions were prepared from Merck standard solutions to a final concentration of 1.000 g/L. Reference solutions were daily prepared by diluting aliquots with pure water and acidified with nitric acid. Buffer solutions were glycine/ hydrochloric acid adjusted at pH 3, acetate buffer at pH 4 to 6, tris-HCl and H2SO4 (Merck) at different concentrations prepared by suitable dilution of the respective concentrated acids in deionizer water. The solutions for study of concomitants effects were prepared in different percentage(m/s) of Na+, K+, Cu++, Mg++, Ba2+by dissolving the irrespective salts in the chloride, sulphates, and phosphoric forms. Solid phase was prepared with ARS resin (Merck), Amberjet-4200 (surface area, 450 m²/g; pore diameter, 450 Å and bead size, and 20-60 mesh) and Dowex-50 was purchased from Aldrich (Milwaukee, USA).

2.2. Instruments

i) An ICP spectrometer (Berken Elmyer model NOVIOS500 SCOTT/Avio 500 ICP –EOS Configuration Part No.810010). A class flow employing argon for plasma in inductively coupled plasma measurements. The instrumental and operational parameters are considered, and the pH value was measured for parameter Mg (II), Mn (II), Zn (II) and Pb (II)

ii) FTIR Nicolet Spectrometer6700 Thermo Scientific Model w1-53711(USA)ElutionofDowex-50

Fig (1): Amberjet-4200

Fig (2): Dowex-50

2.3. Procedure for separation and pre-concentration

ARS resin

Sample volumes from 10 to 50 mL containing up to 200 µg of each cation was transferred to plastic vessels. It was added 10 mL of pH 9.0 ammonium buffer solutions and 0.5 g of the solid phase. The vessel was closed and kept under mechanical stirring for 5 min. The mixture was filtered through a filter paper and the liquid phase was discharged. Solid material retained onto filter paper was washed with 5 mL of 3 mol/L HNO3. Metals ions extracted were then directly determined by ICP. The same procedure was applied to blank sample. An analytical curve prepared in 3 mol/LHNO3 was used in order to avoid matrix effects.

2.4. Procedure for separation and pre-concentration-Dowex-50 resin

Sample volumes from 50 to 200 mL containing up to 50 µg of each cation was transferred to plastic vessels. It was added 10 mL of pH 8.1 ammonium buffer solutions and 0.75 g of the solid phase. The vessel was closed and kept under mechanical stirring for 90 min. The mixture was filtered through a filter paper and the liquid phase was discharged. Solid material retained onto filter paper was washed with 20 mL of2mol/L HNO3. Metals ions extracted were then directly determined by ICP the same procedure was applied to blanks. An analytical curve prepared in 2 mol/LHNO3was used in order to avoid matrix effects.

3. Results and Discussion

In order to obtain quantitative recoveries of Mg (II), Mn (II), Zn (II) and Pb (II) on AmberJet-4200 and Dowex-50 resins the separation and pre-concentration procedures were optimized using an univariate approach for various experimental parameters such as characterization of solid phases, pH, stirring time, sample volume, amounts of solid phase, sorption capacity, and cations desorption from solid phase and concomitants effect.

3.1. Characterization of solid phases

IR spectra Amberjet-4200 and Dowex-50 loaded with Alizarin Red-Shel chelating resins were characterized employing Fourier transform infrared spectrometry (FTIR). The characteristic IR bands (cm⁻¹) for the cationic and anionic resin were: 3503 and 1444 (OH vibrations); 1656 (1, 4-quinonestretching); 1348 (>S=O stretching); and 1275 (>C-Stretching). For ARS loaded Dowex-50, the IR spectrum was analogous but lower intensity is and
deformation bands due to impregnating process agent chelating-resin (ion exchange) were observed. Because of the absence of ion-exchange sites in Amberjet-4200 structure, this sorbent is more able to retain molecule of ARS. The occurrence of five bands further supports the loading of the chelating agent on the resins.

The structures of the resins are represented in figure 3.

![Fig 3: Structures of resins](image)

3.2. Investigated parameters:

Effect of contact time on the removal efficiency of metal ion

Adsorption process was processed for different shaking time of 5, 10, 20, 45, 90, 360, and 1440 minutes, at constant pH, initial concentration, and temperature.

Effect of adsorbent dosage on the removal efficiency

Adsorption process was processed for adsorbent dosage of 0.05, 0.1, 0.15, 0.2, and 0.25 g/l, at constant pH, initial concentration, and temperature.

Effect of pH on the removal efficiency

Adsorption process was processed for different pH values of 2.15, 4.32, 5.3, 6.28, 7.54, and 8.29 at constant contact time, initial concentration, and temperature.

Effect of initial concentrations of metal ion on the removal efficiency

Adsorption process was processed for different initial concentrations of 50, 75, 125, and 150 mg/l at constant pH values, constant contact time, and temperature.

Effect of Temperature on the removal efficiency

Adsorption process was processed for different temperature values of 35, 45, and 55 at constant contact time, initial concentration and dose.

Effect of pH on Mg (II), Mn (II), Zn (II) and Pb (II), sorption

The effect of pH on the % removal of Mg (II), Mn (II), Zn (II) and Pb (II) were studied using treated Amberjet-4200 as adsorbent and compared to that of Dowex-50 as adsorbent. Effect of pH on the chelating efficiency of Amberjet-4200 and Dowex-50 for Mg (II), Mn (II), Zn (II) and Pb (II) was tested by batch experiments using 25 mL of aqueous solutions containing 25 μg of metal ions and 1.0 g of the resins. The pH of the solutions was varied and adjusted in the range 3.0-10.0. Recoveries (%) of Mg (II), Mn (II), Zn (II) and Pb (II) as a function of pH for the Amberjet-4200 and Dowex-50 resins are shown in Figs. 2 and 2, respectively.

Effect of pH

Study on the effect of pH on the % removal of Mg (II), Mn (II), and Zn (II) (Fig. 2) shows that both Zn (II) and Pb (II) exhibit no variation with pH change on the other hand the % removal of Mn (II), increases from 46.952% at pH=2.15 to 99.943% at pH=5.3 . The maximum value of percent removal is found at pH=5.3 this value was kept for further studies.

On using activated carbon as sorbent. Very similar observation was obtained the maximum percent was obtained at pH=5.3 this value was kept for further studies.

![Fig 4: Effect of pH on the removal Mg (II), Mn (II), and Zn (II) by Amberjet-4200](image)

Effect of contact time

Study the effect of time on the removal % of Mg (II), Mn (II), and Zn (II) as in Fig. (5) found that Mg (II), Mn (II), Event remove weak in the beginning when 5 minutes was the removal 50.865% in Mg (II), and 43.987%Mn (II), reaching the maximum value for them at the time of 18 hours was the removal 87.916%, and 74.823%Mg (II), Mn (II), and Zn (II) did not happen was a big change slightly Has been found to remove 87.916% at 18 hours this value was kept for further studies. On the use of activated carbon as absorbent, the obtained very similar observation has been to get the most percent in 87.916% at 18 hours this value was kept for further studies.

![Fig 5: Effect of time on the removal Mg (II), Mn (II), and Zn (II) using Amberjet-4200](image)
Effect of dose

Study on the effect of dose of the removal% of Mg (II), Mn (II), and Zn (II) (Figure 6) shows that both Mg (II), Mn (II), and there are differences and increases with the change in the dose of Mg (II), in the amount of 50.4915% to 0.05gm in the amount of 99.443 0.25gm Mn (II), of 61.232% in the amount of 91.436 % to 0.05gm in the amount of 0.25gm and a simple change in the Zn (II). The maximum value of a percent have been found to remove the amount of 0.25 g This value was kept for further studies. On the use of Amberjet-4200 as absorbent, the obtained very similar observation was obtained maximum 0.25gm percent in dose this value was kept for further studies.

Effect of initial concentration

The effect of initial Mg (II), Mn (II), Zn (II) and Pb (II) ions concentrations ranging (50 – 150 mg/l) on the removal by activated carbons was studied. The results are illustrated graphically in figure 5. A study on the effect of ion concentration in the material removed from both Mg (II), Mn (II), and Zn (II) Figure 7 shows that both Mg (II), Mn (II), and Zn (II) . And the highest removal initially at 50 ppm gave remove the amount of 62.432 % and there was a decrease in the amount of removal greater the concentration until it reached 28.311 % at a concentration of 150 ppm, as well as an element Mn highest removal % 77.707 at 50ppm until it reached a concentration of 69.053% at150 ppm. If the maximum value of 50% to remove ppm kept this value for further studies. On the use of Amberjet-4200 as an absorbent, it has been getting maximum surveillance is very similar 50 ppm per cent in the ion concentration of material kept this value for further studies.

Effect of temperature

In the case of temperature with a fixed quantity and time was found to be the highest and best results Adsorbents for the removal of the three elements are remove In the case of Amberjet-4200 were the removal of the elements as follows of 8.1666% at 35c to 95.2432% at 55c -35.405%at 35c to 90.799%at 55c (Mg – Zn) and a simple change in the Mn. The maximum value of a percent has been found to remove the amount of 55c this value was kept for further studies. On the use of Amberjet-4200 as absorbent, the obtained very similar observation was obtained maximum 55 percent in dose this value was kept for further studies.

Fig (6): Effect of dose on the removal Mg (II), Mn (II), and Zn (II) by Amberjet-4200

Fig (7): Effect of concentration on the removal Mg (II), Mn (II), and Zn (II) by Amberjet-4200

Fig (8): Effect of temperature on the removal Mg (II), Mn (II), and Zn (II) using Amberjet-4200 for removal efficiency

Effect of pH on Mg (II), Mn (II), and Zn (II) sorption

Effect of pH on the chelating efficiency of Amberjet-4200and Dowex-50 for Mg (II), Mn (II), Zn (II) and Pb (II) was tested by batch experiments using 25 mL of aqueous solutions containing 25 μg of metal ions and 1.0 g of the resins. The pH of the solutions was varied and adjusted in the range 3.0-10.0. Recoveries (%) of Mg (II), Mn (II), Zn (II) and Pb (II) as a function of pH for the Amberjet-4200 and Dowex-50 resins are shown in Figs. 1 and 2, respectively.

Effect of the activation time

The effect of the activation time is shown in the Fig. 9. All other activation parameters such as impregnation temperature, impregnation time, impregnation ratio, activation temperature and activation time were kept constant at 120°C, 1.5h, 1.4, 70°C and 1h respectively.

Fig (9): Effect of impregnation time on Amberjet-4200 for removal efficiency of lead (II) at initial concentration of Pb (II) .300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25±2°C.

Effect of the Dowex-50 to KOH activation ratio

The effect of Dowex-50 to KOH activation ratio for EPPAC-1 is presented in figure 5. Activation time and activation temperature were kept constant at 2h and 70C, respectively. In figure 5 it is shown that as the EPPC to KOH activation ratio is increased from 1:0.5 to 1:1 the
removal efficiency of Dowex-50 increases from 54.7% to 57.7% but when the Dowex-50 to KOH activation ratio is increased further up to 1:4 from 1:1 gradual decrease in the removal efficiency of Amberjet-4200 occurs from 57.7% to 38.9%. Thus, it is evident that EPPC to KOH activation ratio significantly affects the removal efficiency of Dowex-50. The optimum Dowex-50 to KOH activation ratio is 1:1 at the activation temperature of 70 °C and activation time of 2h. Actually as the amount of KOH is increased i.e. as the activation ratio is increased from 1:0.5 to 1:1, an increase in the removal efficiency is detected which is due to the fact that greater amount of KOH causes the rate of reaction between Dowex-50 and KOH to increase, due to which the phenomenon of the pore formation also increases.

As the activation temperature is increased from 50 °C to 70 °C, removal efficiency also increases from 46.8% to 57.7%. However, at 80 °C, the removal efficiency is decreased to 54.8%. Initially as the temperature is increased, rate of reaction between activating agent KOH and Dowex-50 is also increased which results in the enhancement of the removal efficiency. Figure (12) shows that at 70 °C, maximum removal efficiency of 57.7% is obtained and this is optimum activation temperature. The increase in the removal efficiency is due formation of porous structure which results in the attainment of high surface area. Also, at lower temperature, the rate of reaction between Dowex-50 and KOH will be slow and thus the removal efficiency is less as compared to removal efficiency obtained at 70 °C [14].

![Effect of pH on cations extraction by Dowex-50 resin](image1)

**Effect of pH on cations extraction by Dowex-50 resin**

Mass of each cation: 50.0 μg. Sample volume: 25 mL. Phase solid mass: 1 g with 0.5% (m/m) ARS. Shaking time: 30 min. Back extraction: 2 extractions with 25.0 mL HNO₃ 6 mol/L.

![Effect of activation temperature on Dowex-50](image2)

**Effect of the activation temperature**

In order to observe the effect of activation temperature on the removal efficiency of Dowex-50, the activation temperature was changed from 50 °C to 80 °C while all other activation parameters such as activation time and activation ratio were kept constant at 2h and 1:1 Dowex-50 to KOH ratio respectively. Figure (12) shows the relationship between the removal efficiency of Dowex-50 and activation temperature.

Choice of eluent

Solutions of sulfuric, nitric, and hydrochloric acids in different concentrations (0.5; 1.0; 2.0; 3.0; 5.0; and 7.0 mol/L) and volumes (1-50 mL) were tested to desorb Mg (II), Mn (II), Zn (II) and Pb (II) from solids phases. It was essential to select an eluent that could also be used for ICP measurements without problems. The best results for quantitative recoveries of the metallic ions were obtained.
using nitric acid as eluent. It was found that 5 mL of 3.0 mol/L HNO3 and 20 mL of 2.0 mol/L HNO3 were sufficient for quantitative (>95%) elution of Mg (II), Mn (II), Zn (II) and Pb (II) in a single step, in the Amberjet-4200 and Dowex-50 resins, respectively.

**Influence of volume of aqueous phase**

Since the volume of solid phase was small compared to the aqueous phase, it was important to study the effect of the latter on the separation and pre-concentration of Mg (II), Mn (II), Zn (II) and Pb (II). The volume of the aqueous phase was varied from 10 to 1000 mL, and the retention was found to be quantitative when the volume of the aqueous phase did not exceed 100 mL, for determination of Mg (II), Mn (II), Zn (II) and Pb (II) using Dowex-50 resin; and 50 mL for determination of Mg (II), Mn (II), Zn (II) and Pb (II) using Amberjet-4200 resin.

**Effect of mass of solid phase**

The mass of solid phase was varied from 0.1 to 1.0 g under optimum conditions. Results demonstrated that 0.50 g and 0.75 g of Amberjet-4200 and Dowex-50 resins, respectively, were sufficient for quantitative retention of Mg (II), Mn (II), Zn (II) and Pb (II).

**Sorption capacity of the solid phases**

Solid phase sorption capacity was also assessed with a multielemental solution. The sorption capacity of the solid phases, Amberjet-4200 and Dowex-50 resins, for Mg (II), Mn (II), Zn (II) and Pb (II) was determined using parameters optimized and a set of solutions containing different amounts of metallic ions in the range of 5-1000 μg/L. Results demonstrated that 0.50 g of Amberjet-4200 resin had a capacity to retain up to 500 μg of Mn (II), and up to 200 μg of Pb (II) and Zn (II). It was observed that 0.75 g of solid phase Dowex-50 was efficient to retain up to 50 μg of each cation.

**Influence of volume of aqueous phase**

Since the volume of solid phase was small compared to the aqueous phase, it was important to study the effect of the latter on the separation and pre-concentration of Mg (II), Mn (II), Zn (II) and Pb (II). The volume of the aqueous phase was varied from 10 to 1000 mL, and the retention was found to be quantitative when the volume of the aqueous phase did not exceed 100 mL, for determination of Mg (II), Mn (II), Zn (II) and Pb (II) using Dowex-50 resin; and 50 mL for determination of Mg (II), Mn (II), Zn (II) and Pb (II) using Amberjet-4200 resin.

**Solid phase’s stability**

Adsorption and desorption were repeated on the same solid phases and adsorptive capacity was estimated after each cycle of operation. The capacity of the Amberjet-4200 resin was also found to be practically constant (within 3-4%) after repeated use six times. For the Dowex-50 resin the results indicated that this could be used only one time.

**Analytical figures of merit and application**

The accurate determination of Mg (II), Mn (II), Pb (II) and Zn (II) at low concentration levels in seawater and physiological solutions after separation and pre-concentration requires Table 2. Comparison of optimized parameters for the two systems studied Parameters Dowex-50 pH value 8.1 9.0 HNO3 (mol/L) for elution 2.0 3.0 HNO3 (mL) for elution 20.0 5.0 Loading time (min) 90 5 Quantity of solid phase (g) 0.75 0.50 Adsorptive capacity (mg/L) 50 Mn (II), 500 Zn (II) and Pb (II): 200 Preconcentration factor Zn (II) and Pb: 5 Zn (II): 50 Mn (II), and Cu (II): 10; Limit of detection (μg/L) Mn (II): 25; Zn (II): 23; and Pb (II): 9 Mn (II): 32; Zn (II): 29; Limit of quantification (μg/L) Mn (II): 82; Zn (II): 76; Mn (II): 105; Zn (II): 98

**Table (1): Different parameters of Amberjet-4200 and Dowex-50.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Amberjet-4200</th>
<th>Dowex-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value</td>
<td>8.1</td>
<td>9.0</td>
</tr>
<tr>
<td>HNO3 (mol/L) for elution</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Loading time (min)</td>
<td>90</td>
<td>5</td>
</tr>
<tr>
<td>Quantity of solid phase (g)</td>
<td>0.75</td>
<td>0.50</td>
</tr>
</tbody>
</table>

**4. Conclusion**

As indicated in the result obtained. The present paper is focused on the removal efficiency of synthetic resin as Amberjet-4200 and Dowex-50 depending upon analytical measurements of trace analysis of west water matrices by Inductively Coupled Plasma, and the fact that Mg (II), Mn (II), Zn (II) and Pb (II) are trace constituents, in wastewater samples. Two procedures using chelating resins obtained by modification of nonionic polymer sorbent Amberjet-4200 and anion exchanger Dowex-50 with AR are proposed for separation and preconcentration of Mg (II), Mn (II), Zn (II) and Pb (II) from wastewater matrices. The procedures developed are simple and efficient. The system Dowex-50 presented some advantages due to rapid kinetic, low consumption of reagents and eluent, good stability and a good enrichment factor (up to 50 as for Zn). The sorption capacity and pre-concentration factor of ARS loaded in Amberjet-4200 are higher than the ARS loaded in Dowex-50. Furthermore, the elution step does not involve the use of organic solvents as other procedures. The addition recovery experiments showed that the proposed procedures had proper accuracy. The proposed method is simple and suitable for the separation and determination of Mg (II), Mn (II), Zn (II) and Pb (II) in wastewater samples.

**References**


