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(ARTICLE)

Determination Of Concentration Of Some Pollution Cations, Antions And Metals In The Groundwater Of Area Tiji In Libya

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تحديد تركيز بعض الكاتيونات والأنيونات والمعادن الملوثة في المياه الجوفية بمنطقة تيجي في ليبيا

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Abstract

Water is the world's most vital natural resource, essential for sustaining all forms of life and promoting economic and societal development. The aims of this research are to determine whether the concentrations of some cations, anions, and metals of the Tiji groundwater are above safe limits, which would indicate they may be potential polluters, to explore the presence of the chemical elements and their likely environmental and health impacts, to raise awareness among the community of the risks of consuming untreated groundwater and encourage ongoing water quality monitoring, to explore cost-effective and effective chemical treatment technologies ion exchange and polymer-based chelating processes of removing polluting substances from groundwater, to assist future planning of sustainable water management strategies for arid regions like Tiji. Experimental study was conducted on groundwater samples collected from three representative wells in the Tiji region, Libya (wells at approximately 30 m and 120 m depths as indicated in the study site selection. The results indicate that the groundwater in the Tiji region is mineral-hard and chemically hard with high levels for sulfate, chloride, hardness, and TDS, rendering it unfit to be consumed directly by humans without treatment. Exper-imental and analytical data strongly confirm Hypothesis 1 (H1). The high initial sulfate and chloride levels in the groundwater warrant the need for selective removal, and the ion exchange process. Hypothesis 2 (H2) holds well, i.e., AnaLig ME-0_2 chelating resin have very good adsorption efficiency of Lead and mercury. Installation of a complete water treatment system with anion exchange resins is recommended for effective reduction of sulfate and chloride levels.

Keywords: Concentration, Pollution Cations, Antions, Metals, Groundwater, Libya

المخلص

يُعدّ الماء أهم مورد طبيعي في العالم، فهو ضروري لاستدامة جميع أشكال الحياة وتعزيز التنمية الاقتصادية والاجتماعية. تهدف هذه الدراسة إلى تحديد ما إذا كانت تركيزات بعض الكاتيونات والأنيونات والمعادن في المياه الجوفية في تيجي تتجاوز الحدود الآمنة، مما قد يشير إلى أنها ملوثات محتملة، واستكشاف وجود هذه العناصر الكيميائية وتأثيراتها البيئية والصحية المحتملة، ورفع مستوى الوعي لدى المجتمع بمخاطر استهلاك المياه الجوفية غير المعالجة، وتشجيع المراقبة المستمرة لجودة المياه، واستكشاف تقنيات المعالجة الكيميائية الفعالة من حيث التكلفة، مثل التبادل الأيوني وعمليات التخليب القائمة على البوليمرات، لإزالة المواد الملوثة من المياه الجوفية، والمساعدة في التخطيط المستقبلي لاستراتيجيات إدارة المياه المستدامة للمناطق القاحلة مثل تيجي. أُجريت دراسة تجريبية على عينات من المياه الجوفية جُمعت من ثلاث آبار نموذجية في منطقة تيجي، ليبيا (آبار على عمق 30 مترًا و120 مترًا تقريبًا، كما هو موضح في اختيار مواقع

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الدراسة). تشير النتائج إلى أن المياه الجوفية في منطقة تيجي عسيرة معدنيًا وكيميائيًا، مع مستويات عالية من الكبريتات والكلوريدات والصلابة ومجموع المواد الصلبة الذائبة، مما يجعلها غير صالحة للاستهلاك البشري المباشر دون معالجة. تؤكد البيانات التجريبية والتحليلية بقوة الفرضية الأولى (H1). تستدعي المستويات الأولية المرتفعة للكبريتات والكلوريدات في المياه الجوفية الحاجة إلى إزالة انتقائية، وعملية التبادل الأيوني. وتؤكد الفرضية الثانية (H2) صحة النتائج، حيث يتمتع راتنج AnaLig ME-02 المخلبي بكفاءة امتصاص عالية جدًا للرصاص والزئبق. يُوصى بتركيب نظام متكامل لمعالجة المياه باستخدام راتنجات التبادل الأيوني لخفض مستويات الكبريتات والكلوريدات بشكل فعال.

الكلمات المفتاحية: التركيز، التلوث، الكاتيونات، الأنيونات، المعادن، المياه الجوفية، ليبيا.

Introduction

Water is the most vital natural resource on earth, required for survival of all forms of life and support of economic and social development. Surface water resources are limited in most parts of the world's arid and semi-arid regions, such as Libya, and populations depend to a large degree on groundwater as their principal source of drinking water. Groundwater quality therefore becomes one of the most important determinants of the safety and sustainability of this resource for domestic as well as agricultural use. Groundwater geochemistry is governed by the geology of the aquifer, the composition of the soil and rock it infiltrates, and anthropogenic input from industrial effluent, agricultural runoff, and indiscriminate waste disposal. These sources may introduce many pollutants like cations, anions, and heavy metals into the subsurface water system.1

Groundwater quality includes its physical, chemical, and biological properties. Its physical properties include taste, odor, turbidity, and temperature, though since groundwater is usually colorless, odorless, and tasteless, the chemical and biological aspects are of greatest importance in determining if it is potable and its quality. Chemically, groundwater contains a mix of dissolved solids that can be grouped into three general categories: major constituents, minor constituents, and trace elements. The total of all these dissolved components is referred to as the Total Dissolved Solids (TDS) and provides the overall water purity measure. Dissolved solids in any natural water system are present either as positively charged ions (cations) or negatively charged ions (anions). The ions exist in such a way that the total positive charge is always neutralized by the total negative charge, leading to electrochemical equilibrium of the system. 2

To understand how these ions behave and can be treated in water treatment facilities, it is appropriate to put into perspective the concept of ion exchange. It is a technique in which the substitution of unwanted ions in water with more desirable ones is achieved by using ion exchange resins, special materials. Figure 1 shows how cation exchange resins exchange unwanted cations such as sodium (Na^+) for hydrogen ions (H^+), and anion exchange resins exchange anions such as chloride (Cl^-) for hydroxide ions (OH^-). As H^+ and OH^- unite, water molecules (H_2O) are formed, and pure water is the outcome. This metabolic reaction, known as metathesis, is the chemical basis for the use of ion exchange and chelating polymers to cleanse water. 1

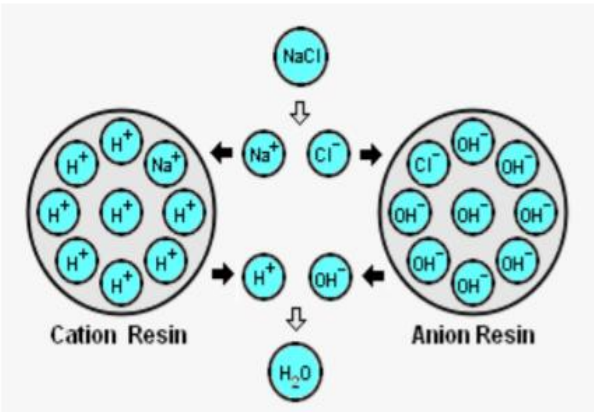

Figure 1. Process of Metathesis Occurs on Cation and Anion Exchanging Beds3

Tiji area in Libya, which is found in the northwestern region of the country, depends on groundwater as the sole source of potable water. Groundwater abstraction has been more pronounced due to increased utilization for agriculture and domestic use, leading to quantitative depletion and qualitative deterioration. High salt and heavy metal concentrations in groundwater present major risks to public health. In order to assist in addressing these problems, samples were taken from several wells in Tiji and subjected to analysis to determine the concentrations of the major pollutant ions and metals like chlorides (Cl^-), sulfates (SO_4^{2-}), mercury (Hg), and lead (Pb). 4

Table 1 showed that the water is of good quality and drinking water standard. A pH level of 7.54 indicates neutral to slightly alkaline, which is ideal for human consumption. The Total Dissolved Solids (TDS) and the electrical conductivity of 332 mg/L and 665 µS/cm, respectively, remain within limits, implying that the content of minerals dissolved is not high. The Total Hardness of 180 mg/L indicates moderate hardness, which is usual in natural water containing plenty of minerals such as Calcium (48.1 mg/L) and Magnesium (12.7 mg/L). The concentration of Sodium (28.6 mg/L) and Potassium (1.8 mg/L) is relatively low, and inorganic ions such as Chloride (44.0 mg/L), Sulfate (31.0 mg/L), Nitrate (2.1 mg/L), and Fluoride (0.3 mg/L) are all within the WHO limit. Overall, this water has a good mineral content, is free from harmful contaminants, and is suitable for drinking as a source of quality drinking water.

Table 1. Water Sample of Department of Laboratories & Technical Development (Chemistry Section)

No	Parameter	Unit	Result	Test Method
1	pH	–	07.54	APHA 4500-H^+ B
2	Electrical Conductivity	µS/cm	665	APHA 2510 B
3	Total Dissolved Solids (TDS)	mg/L	332	APHA 2540 C
4	Total Hardness (as $CaCO_3$)	mg/L	180	APHA 2340 C
5	Calcium (Ca^{2+})	mg/L	48.01.00	APHA 3500-Ca B
6	Magnesium (Mg^{2+})	mg/L	12.07	APHA 3500-Mg B
7	Sodium (Na^+)	mg/L	28.06.00	APHA 3500-Na B
8	Potassium (K^+)	mg/L	01.08	APHA 3500-K B
9	Chloride (Cl^-)	mg/L	44.00.00	APHA 4500-Cl B
10	Sulphate (SO_4^{2-})	mg/L	31.00.00	APHA 4500-SO_4 E
11	Nitrate (NO_3^-)	mg/L	02.01	APHA 4500-NO_3 B
12	Fluoride (F^-)	mg/L	00.03	APHA 4500-F D

Table 2 showed the quality of groundwater from a well with a depth of 36 meters (Well Gasa) that was analyzed at the Water Quality Laboratory in Malang on January 29 – February 10, 2013, overall the physical and chemical parameters are still in decent ranges for groundwater. The Turbidity reading of 6.7 NTU indicates a very acceptable level of water clarity, while the Total Dissolved Solid (TDS) reading of 827 mg/L is still lower than the WHO-potable water standard (1,000 mg/L). The test results indicate that the groundwater quality is extremely good and can be used for domestic use, although constant monitoring has to be performed to maintain the balance of the mineral content and prevent future additions of chemical substances or heavy metals.

Table 2. Results of Water Quality

No	Parameter	Unit	Result	Method of Analysis	Remark
1	Turbidity	NTU	6.7	QXL/AXN (Electrometer)	-
2	Total Dissolved Solid (TDS)	mg/L	827	QXL/AXN (Gravimetry)	-
3	Total Suspended Solid (TSS)	mg/L	0.2	APHA 2540-D-2005	-
4	Colour	TCU	25	APHA 2120-C-2005	-
5	Sulfide (S)	mg/L	2550	APHA 4500-S^2-2005	-
6	Sodium (Na^+)	mg/L	319	APHA 3500-Na-B-2005	-
7	Potassium (K^+)	mg/L	7.59	APHA 3500-K-B-2005	-
8	Calcium (Ca^{2+})	mg/L	71.6	APHA 3500-Ca-B-2005	-
9	Magnesium (Mg^{2+})	mg/L	9,67	APHA 3500-Mg-B-2005	-
10	Chloride (Cl^-)	mg/L	17,05	APHA 4500-Cl-B-2005	MDL < 0.0005
11	Nitrate (NO_3^-)	mg/L	0.02	APHA 4500-NO_3^--B-2005	MDL < 0.0005
12	Iron (Fe)	mg/L	0.19	APHA 3111-B-2005	MDL < 0.0290
13	Copper (Cu)	mg/L	0.006	APHA 3111-B-2005	MDL < 0.0028
14	Cadmium (Cd)	mg/L	0.001	APHA 3111-B-2005	MDL < 0.0020
15	Mercury (Hg)	mg/L	0.0003×10^{-3}	APHA 3111-B-2005	-
16	Lead (Pb)	mg/L	0.002	APHA 3111-B-2005	MDL < 0.0025

No	Parameter	Unit	Result	Method of Analysis	Remark
17	Zinc (Zn)	mg/L	0.03	APHA 3111-B-2005	MDL < 0.0031
18	Sulphate (SO_4^{2-})	mg/L	92.6	APHA 4500-SO_4^{2-}-E-2005	-
19	Fluoride (F^-)	mg/L	10.7	APHA 4500-F^--D-2005	-
20	Silica (SiO_2)	mg/L	10.1	APHA 3111-B-2005	MDL < 0.1011

Based on UKM UNIPEQ mineral water sample analysis results (Table 3), Universiti Kebangsaan Malaysia, the water is good qualitatively in its physical and chemical properties and is safe to drink. A pH of 7.88 indicates neutral to alkaline water conditions, within the optimum range for drinking water. Practically nil turbidity of 0.77 NTU and Total Suspended Solids (TSS) of 0.05 mg/L indicate very clear water. 289 mg/L TDS level is even lower than the upper limit suggested by WHO (500 mg/L). The results of the test therefore confirm that sample water is within the safety limits of safe mineral water as well as high nutritional value of minerals.

Table 3. Results of analysis of mineral water samples

No	Parameter	Unit	Result	Test Method
1	pH	–	7.88	APHA 4500-H^+ B (Meter)
2	Turbidity	NTU	0.77	APHA 2130 B (Turbidity Meter)
3	Total Dissolved Solids	mg/L	289	APHA 2540 C
4	Total Suspended Solids	mg/L	0.05	APHA 2540 D
5	Total Chromium (Cr)	mg/L	0.001	Merck Method 8036 / AAS-50-Cr(G)
6	Mercury (Hg)	mg/L	0.0001	Microwave Digestion / ICP-MS
7	Arsenic (As)	mg/L	0.001	Microwave Digestion / ICP-MS
8	Lead (Pb)	mg/L	0.001	Microwave Digestion / ICP-MS
9	Cadmium (Cd)	mg/L	0.001	Microwave Digestion / ICP-MS
10	Copper (Cu)	mg/L	0.07	Microwave Digestion / AAS
11	Zinc (Zn)	mg/L	0.18	Microwave Digestion / AAS
12	Nickel (Ni)	mg/L	0.01	Microwave Digestion / AAS
13	Manganese (Mn)	mg/L	0.02	Microwave Digestion / AAS
14	Iron (Fe)	mg/L	1.41	Microwave Digestion / AAS
15	Sodium (Na)	mg/L	480.0	Microwave Digestion / AAS
16	Magnesium (Mg)	mg/L	123.1	Microwave Digestion / AAS

By combining the results from the individual laboratories, the research attempted to determine a clear impression of the scale and nature of groundwater pollution in the Tiji area. Some ions and heavy metals' content had marked variations between the wells, as indicated by the results. As shown in Table 4, chloride concentration was as much as 2880 mg/L at a depth of 30 meters in Well Gaza, far exceeding World Health Organization (WHO) guideline of 250 mg/L. Sulfate concentration was also as much as 3550 mg/L, indicating high salinity that renders the water unsuitable for drinking without treatment. The presence of mercury (Hg) and lead (Pb), although in smaller quantity, is problematic given their toxicity and bioaccumulation potential. Lead concentrations ranging to 0.07 mg/L were recorded in Well Shnina and exceeded the permissible concentration of 0.05 mg/L, while mercury was recorded at 0.03 mg/L thirty times safe level.

Table 4. Focus problem of chemical elements

Chemical elements	Water Quality Standards	Well depth of 30 M Well Gaza	Well depth of120 M Well Abukhlida	Well depth of 120 M Well Shnina	Until
Cl	250	2880	355	-	Mg/L
So_4	250	3550	476	-	Mg/L
Hg	0.001	-	-	0.03	Mg/L
Pb	0.05	-	-	0.07	Mg/L

These observations highlight the need for the development of cost-saving and saving treatment technology to improve the quality of groundwater. The application of chelating resins and ion exchange is among the possible solutions, where such resins can be used to selectively remove unwanted ions and heavy metals from water. For example, anion exchange resins trap the sulfate and chloride ions extremely effectively, while chelating resins such as AnaLig ME-02 have demonstrated immense adsorption capability for metals such as lead and mercury. By employing these processes together, there can be an overall treatment system treating both ionic and metal impurities simultaneously. 5

The main objectives of the current study are thus:

1. To determine whether concentrations of certain cations, anions, and metals in Tiji groundwater exceed safe concentrations, which would indicate pollution.
2. To investigate the distribution of these chemical species and their possible environmental and health implications.
3. To raise awareness of the people on the risks of consuming untreated groundwater and encourage frequent water quality analysis.
4. To explore low-cost and effective chemical treatment technologies particularly ion exchange and polymer-based chelating process of purifying pollutants from groundwater.
5. To contribute to the development of future sustainable water management strategies in arid regions like Tiji.

The scope of this research is comprised of two broad elements. The first is the description and chemical assessment of groundwater from three wells in the Tiji area, establishing the concentration of significant contaminants. The second assesses chemical treatment processes, like ion exchange and chelation, for reducing levels of contaminants. Through the unification of the two, the research presents both a diagnostic and remedial solution to groundwater contamination. 6

Groundwater quality survey in Tiji, Libya is an important ecological issue directly related to public health and community sustainability. Quantitative data as provided by Figures 1 through 4 and Table 1 indicate that a number of water samples are above international standards, and it is a sincere situation in need of urgent attention. With the application of scientific knowledge and technological technologies such as ion exchange and polymer-based resins, rehabilitation of the groundwater quality is probable, coupled with safeguarding the health of communities and establishing confidence in sustainable exploitation of water resources in the region. 7

2. Literature Review

2.1. Sulfate and chlorideTreatments

There are also different methods for the removal of sulfate (SO_4^{2-}) and chloride (Cl^-) ions from water, each with differing efficacy, cost, and applicability according to the concentration of impurities and quantity of water to be treated. These common treatment techniques are ion exchange, reverse osmosis (RO), electrodialysis, and chemical precipitation. In ion exchange, there are also specific anion exchange resins that swap sulfate and chloride ions with superior ions, typically hydroxide (OH^-), that proceed to combine with hydrogen ions (H^+) to yield good-quality output water. It is very effective for small- and medium-scale water treatment and yields good-quality output but requires periodic resin renewal. Reverse osmosis, on the contrary, employs a semi-permeable membrane that separates water from sulfate and chloride ions under pressure. 8

It is one of the most effective desalination and purification technologies, but with higher operating costs and energy needs. Electrodialysis employs electrical potential to drive ions through selective membranes, being highly effective in reducing sulfate and chloride levels in relatively brackish water. Sulfate can also be eliminated by chemical precipitation with barium or calcium salts by forming insoluble compounds. Method choice is a function of the conditions at the site, cost, and water purity to be achieved in treatment. 9

2.2. Ion Exchange

Ion exchange is the most effective and commonly used method for the removal of large quantities of sulfate from municipal and industrial water supplies. It is less frequently applied, however, to single-family dwelling treatment due to its high cost, maintenance requirements, and requirement for special equipment. In this process, ions within the water are replaced with ions of the same sign that are attached to a resin material. For example, sulfate (SO_4^{2-}) ions in the water are exchanged for hydroxide (OH^-) ions of an anion exchange resin, whereas cationic impurities can be replaced by hydrogen (H^+) or sodium (Na^+) ions depending upon the system type. 10

We all know about water softeners, a simple and common type of ion exchange equipment which is essentially designed for removing calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions for hardness. The technology is similarly applied to remove sulfate and other anions from water. Efficiency of ion exchange depends on the pH of the water, ionic strength, and selectivity of the resin. The capacity needs to be replenished by periodic resinning with acid solution or salt. Generally, ion exchange provides a high-quality, controlled, and stable process for desulfurization of water that is sulfate-rich. 11

2.3. Anion Enxhange Resin

Anion exchange resin is a medium that is used to remove negatively charged ions (anions) such as sulfate (SO_4^{2-}), chloride (Cl^-), nitrate (NO_3^-), and fluoride (F^-) from water (Figure 2). Anion exchange resin operates based on the ion exchange process in which unwanted anions in water are substituted with less harmful ions usually hydroxide (OH^-) pre-charged on the resin. When water passes through the resin bed, the water's anions attach to the resin, displacing hydroxide ions from their place, which, along with hydrogen ions (H^+) from an ion exchange resin or water itself, yield pure H_2O. 12

Anion exchange resins are composed of synthetic, insoluble polymer beads that contain active sites having posi-tively charged func-tional groups, for example, quaternary am-monium. The functional sites have the ability to attract and trap anions that are negatively charged. Anion exchange resins can broadly be classified as strong base resins that trap all types of anions including weak acids, and weak base resins, useful for strong acid anions like sulfate and chloride. 13

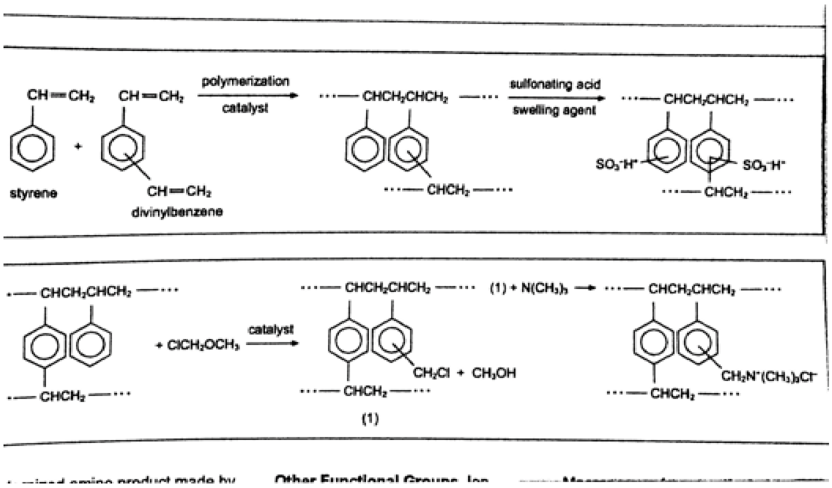

Figure 2. Anion Enxhange Resin

2.4. Removal heavy metals

Chelating resins are heavy resins utilized for the removal of heavy metals such as lead (Pb^{2+}), mercury (Hg^{2+}), cadmium (Cd^{2+}), copper (Cu^{2+}), and zinc (Zn^{2+}) from contaminated water. Unlike typical ion exchange resins that adsorb ions primarily by charge ex-change, chelating resins adsorb ions by a typical co-ordination or complexation reaction (Figure 3). In the process, functional groups of resin often nitrogen-, oxygen-, or sulfur-containing donor atoms establish stable covalent coordinate linkages with metal ions. Chelation, a result of this, allows target metal ions to be selectively and firmly bound by the resin despite the presence of competing ions. 14

As a result of this selectivity, chelating resins are especially useful for the removal of industrial wastewater, ground-water, and chemical process streams containing trace levels of toxic metals. AnaLig ME-02 resin is one such case that has shown superior ad-sorption capacity for lead and mercury ions due to its aggressive chelating functional groups. After saturation, the resin can be regenerated using acid or complexing solutions to release the bound metals, making it reusable. Chelating resins, in general, offer a cheap, efficient, and eco-friendly means of heavy metal removal, ensuring water safety and environmental compliance. 15

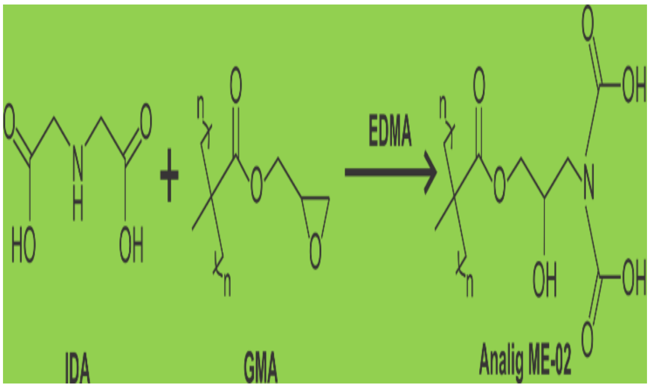

Figure 3. Removal heavy metals

2.5. Chelating resin

AnaLig ME-02 is a professional chelating resin for selective adsorption of toxic heavy metal ions such as lead (Pb^{2+}) and mercury (Hg^{2+}) from aqueous solutions. The reason why the resin is effective lies in its unique chemical structure that consists of a polymer support a cross-linked polystyrene or methacrylate backbone and functionalized with selective chelating ligands containing donor atoms such as nitrogen, oxygen, and sulfur. These donor atoms establish coordinate covalent bonds with metal ions and generate very stable chelate complexes. 16

Preparation of AnaLig ME-02 is normally a multi-step process involving chemical modification. The polymer matrix is preformed through suspension polymerization to produce high surface area and mechanically robust spherical resin beads. The bead surface is chemically modified by incorporating reactive groups such as amine, carboxyl, or thiol groups. Selective chelating ligands are grafted or immobilized on the resin surface through covalent attachment to enhance its selectivity for target metal ions. 17

2.6. Hypothesis

Anion Exchange Resin has capable of absorbing Sulfate and chloride.

Groundwater pollution by dissolved salt and heavy metals is an environmental problem of great concern, especially in arid regions like Tiji, Libya, where groundwater is greatly used as the primary source of drinking water. Sulfate (SO_4^{2-}) and chloride (Cl^-) in high concentrations will result in excessive water salinity, corrosion of pipes, and poisonous human health effects, whereas lead (Pb^{2+}) and mercury (Hg^{2+}) are poisonous due to their persistence in the environment, bioaccumulation, and toxicity. Therefore, effective and cost-free treatment technologies need to be employed in order to remove these contaminants from groundwater. 18

Ion exchange is perhaps the most sophisticated method of water purification. It relies on the use of anion exchange resins containing positively charged functional groups that trap and exchange harmful anions with less harmful ones. These resins are particularly renowned for their ability to remove sulfate and chloride ions. Based on the fundamental principles of ion exchange and previous studies on resin selectivity, Anion Exchange Resin is expected to adsorb chloride and sulfate ions from contaminated groundwater. 19

H1: Anion Exchange Resin is capable of absorbing sulfate and chloride ions

AnaLig ME-02 chelating resin has exellent ability adsorption of Lead and mercury

While chelating resins operate on a different principle based on the formation of coordinate covalent bonds involving the specific functional groups on the resin and target metal ions, AnaLig ME-02 is a chelating polymer employed for the selective adsorption of heavy metal ions such as lead and mercury. Its molecular structure contains functional ligands capable of building stable complexes with such metal ions even at low levels of concentrations. Such selectivity makes AnaLig ME-02 extremely good at toxic metal removal compared to conventional ion exchange resins. It is therefore presumed that AnaLig ME-02 chelating resin has very high adsorption ability towards lead and mercury ions. 20

H2: AnaLig ME-02 chelating resin has excellent adsorption ability for lead and mercury ions

3. Methodology

Experimental experiments were carried out using groundwater samples from three representative wells in the Tiji area, Libya (wells of approximately 30 m and 120 m deep as indicated in the selection of the study site) (Figure 4). Sampling in the field was standard procedure: wells were purged by pumping at least three well volumes prior to sampling in order to recover fresh formation water, and the recovered samples were transferred into previously cleaned polyethylene bottles. Metal analysis samples were acidified during collection to pH <2 using ultrapure nitric acid in order to preserve dissolved metal; anion analysis samples were held unacidified and refrigerated (4°C) during transport. Samples were labeled, iced, and forwarded to analytical laboratories (local Libyan laboratory and collaborating laboratories at UKM and Malang) for analysis within suggested holding times. Chain-of-custody and sample documentation were included in each batch, and triplicate samples, method blanks, and certified reference material were spiked for QA/QC (Figure 5).

Figure 4. Location of the Research

Analytical measurements integrated field measurements with laboratory instrumentation. Field instrumentation in-cluded a calibrated portable pH meter, conductivity probe, and thermometer to monitor in-situ values. Chloride and sulfate concentrations were determined in the laboratory by ion chromatography (IC) or by standard ti-trimetric procedures (ar-gentometric titration for chloride or gravimetric/turbidimetric or IC for sulfate) as equipment allows. Heavy metals (mercury and lead) were determined by atomic absorption spectroscopy by graphite furnace or cold-vapor for mercury, or by in-duc-tively coupled plasma mass spectrometry (ICP-MS) if available. Multi-point standard and procedure blanks were used for analytical calibration; recovery tests with spiked samples and duplicate runs ensured method consistency. Detection limits and method precision were documented and verified against certificate-of-analysis results from collaborating laboratories. 21

For evaluating remediation performance, bench-scale experiments tested two treatment programs: (1) anion exchange using a commercially available strong-base anion exchange resin and (2) selective removal of heavy metals using AnaLig ME-02 chelating resin. Batch and fixed-bed column tests were performed. Measured volumes of groundwater (250–500 mL) were mixed with known weights of resin (resin dose range: 0.5–10 g/L) in sealed flasks and agitated at controlled temperature (20–25°C). Control Bulk Aquifer Tests (BATs) were evaluated to determine the long-term effectiveness of remediation. Contact time was varied (30 min to 24 h) to test kinetic behavior. Effect of pH (regulated by addition of dilute HCl or NaOH), ionic strength, and competing ions was tested by preparing solutions that mimic field ionic composition. The samples were filtered and analyzed for residual chloride, sulfate, lead, and mercury to determine percent removal and adsorption capacity (mg/g) at equilibrium. 22

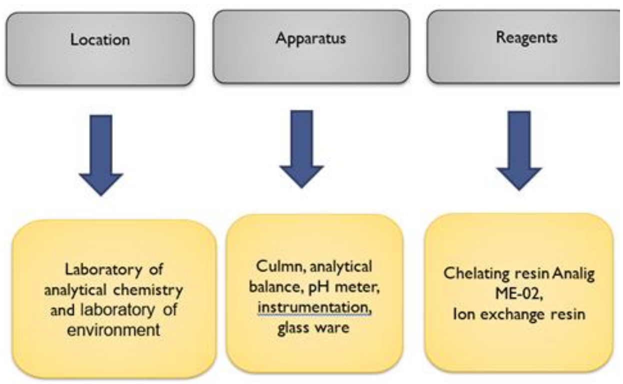

Figure 5. Research Method

Fixed-bed (column) experiments used glass columns (internal diameter ~2.5 cm, bed depths 10–30 cm) to simulate continuous flow treatment. Resin beds were pre-conditioned and regenerated according to the manufacturer's advice (e.g., NaCl or NaOH for anion resins; acid or complexant for chelating resins). Groundwater was forced upward or downward at controlled flow rates (e.g., 1–10 mL/min), and effluent was sampled at regular intervals to construct breakthrough curves and determine bed capacity and service life. Regeneration cycles were run to study resin recycle and recoverability of the adsorbed metals; regenerant solutions were sampled to estimate mass balance and recovery of the metal. 23
Statistical treatment of all the experimental data was performed. Langmuir and Freundlich isotherms and kinetic models (pseudo-first- and pseudo-second-order) were employed to model experimental data to determine mechanisms of adsorption. Removal efficiencies were correlated against WHO and national water quality standards. A combination of sampling in the field, strong laboratory analysis, and controlled column- and bench-scale testing provided a comprehensive evaluation of (i) levels of contamination in

Tiji groundwater and (ii) practical effectiveness of anion exchange and AnaLig ME-02 chelating resin for sulfate, chloride, lead, and mercury removal. 24

4. Result and Discussion

4.1. Result

Table 5 indicates the result of physicochemical analysis of Tiji groundwater samples from Libya and their comparison with Moroccan Standard NM 03.7.001 (2008) for drinking water quality. Parameters that are involved are pH, total dissolved solids (TDS), total hardness (TH), alkalinity, concentration of carbonate and bicarbonate, major anions (sulfate and chloride), and major cations (calcium, magnesium, sodium, and potassium). The analytical methods for each parameter are also provided, founded on globally accepted standards such as ISO and Standard Methods (SM).

The analysis shows that the groundwater pH is 7.08, which falls in the acceptable range of 6.5–8.5 and makes the water slightly neutral and acceptable from the alkalinity or acidity standpoint. However, TDS content (1665 mg/L) exceeds the desirable limit of 1200 mg/L and is a reflection of high mineral content and likely salinity with possible impacts on taste and acceptability for household use. Similarly, total hardness (720 mg/L) far exceeds the permissible level of 500 mg/L and the water is extremely hard, largely because of high calcium (280 mg/L) and magnesium (64.8 mg/L) contents.

It also contains alkalinity (200 mg/L) and bicarbonate (244 mg/L) with a moderate buffering capacity but no carbonates (CO_3). Both sulfate (SO_4^{2-}) and chloride (Cl^-) at 475.5 mg/L and 345.5 mg/L, respectively, were higher than their standard values of 250 mg/L. This indicates probable contamination due to dissolution of natural minerals or anthropogenic sources such as agricultural runoff or industrial wastewater. Excessive sulfate concentrations can cause taste and laxative effects, while excessive chloride concentrations can cause corrosion and salinity issues.

The cations, sodium (Na^+) and potassium (K^+), were present at concentrations of 198 mg/L and 10 mg/L, respectively. The concentration of sodium is nearly at the upper desirable limit of 200 mg/L, which is objectionable for individuals on low-sodium diets or those suffering from medical conditions such as hypertension. Potassium, though present in very small amount, is still within safe limits.

Table 5. Result of Analysis

Test	Result	Standard Limit (per Moroccan Standard NM 03.7.001 - 2008)	Test Method
pH	7.08 (at 17.9°C)	6.5 – 8.5	L.NCISM ISO (10523) 1994 Edition 2006
Total Dissolved Solids (T.D.S) at (105°C) mg/L	1665	1200	S.M 2540 B:1998
Total Hardness (T.H) mg/L	720	500	L.NCISM ISO (6059) 1984 Edition 2006
Alkalinity (T.A) mg/L	200	-	L.NCISM ISO (996-1) Edition 2006
Carbon Trioxide (CO3) mg/L	Nil	-	L.NCISM ISO (996-3) 1994 Edition 2006
Bicarbonates (HCO_3) mg/L	244	-	L.NCISM ISO (996-3) 1994 Edition 2006
Sulfates (SO_4^{2-}) mg/L	475.5	250	S.M 2500-SO_4^{2-} C:1998
Chlorides (Cl^-) mg/L	345.5	250	L.NCISM ISO (9297) 1998 Edition 2006
Calcium (Ca^{2+}) mg/L	280	200	L.NCISM ISO (6058) 1984 Edition 2006
Magnesium (Mg^{2+}) mg/L	64.8	-	L.NCISM ISO (6059) 1984 Edition 2006
Sodium (Na^+) mg/L	198	200	L.NCISM ISO (996-3) Edition 2006
Potassium (K^+) mg/L	10	-	L.NCISM ISO (996-3) Edition 2006

4.2. Discussion

4.2.1. Anion Exchange Resin has capable of absorbing Sulfate and chloride

The analytical results shown in Table 2 clearly show that the Libyan Tiji area groundwater sample contains high concentrations of sulfate (SO_4^{2-}) and chloride (Cl^-) ions. These two values, 475.5 mg/L for sulfate and 345.5 mg/L for chloride, exceed the Moroccan Standard NM 03.7.001 (2008) acceptable limit of 250 mg/L for both ions. They reflect a significantly elevated degree of mineralization and possible contaminants in the groundwater system. Such a condition is of public health and environmental concern, and anion exchange resin technology is the suitable and effective treatment technology to improve water quality. 25

High Sulfate and Chloride Concentrations

Chloride and sulfate ions are the most common anions found in natural water. Their magnitude varies with geologic structures, evaporation, and anthropogenic sources such as fertilizer application, industrial effluent, and disposal of sewage effluent. In Tiji groundwater, the elevated sulfate concentration could be due to dissolution of sulfate-bearing minerals such as gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$) from aquifer rocks. Similarly, chloride content is usually found to be related to dissolution of halite (NaCl) or intrusion impact of saline water, particularly in arid environments where recharge of groundwater is nil. 26

Sulfate in excess in potable water leads to taste issues and acts as a laxative, particularly when accompanied by magnesium or sodium. Chloride, however, gives water a salty flavor and contributes to the corrosion of plumbing fixtures, water heaters, and appliances. Above all, the combined high concentrations of these anions also further increase the Total Dissolved Solids (TDS) content 1665 mg/L in this study which reduces the potability and usability of water for residential or industrial applications further. All these conditions stand testimony to the compelling need for such a cost-effective ion removal process as anion exchange (Figure 6). 27

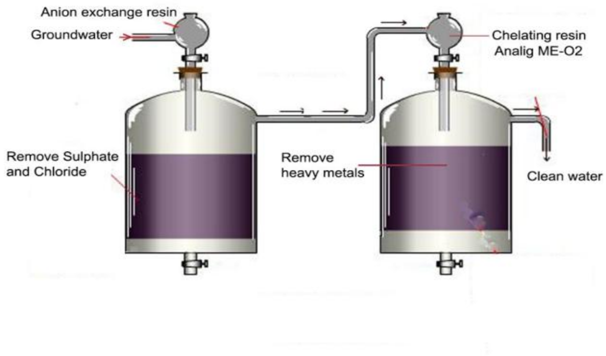

Figure 6. Ion exchange process27.

Principle and Mechanism of Anion Exchange Resin

Anion exchange resins are man-made polymeric beads that possess positively charged functional groups which are capable of attracting and exchanging negatively charged ions (anions) in the water. The mechanism is an electrostatic attraction of the fixed cationic groups of the resin to the anions in the water. In traditional applications, the resin initially holds hydroxide (OH^-) or chloride (Cl^-) ions, which are readily interchangeable with sulfate, nitrate, or any other target anions that might be present in the contaminated water.28 The overall reaction for sulfate removal is presented below:

$$R–Cl + SO_4^{2-} \rightarrow R_2–SO_4 + 2Cl^-$$

where R is the resin matrix. Sulfate ions replace chloride ions bonded to the resin up to the saturation of the resin in this process. The resin is regenerated by washing it with a salt (NaCl) or an alkaline (NaOH) solution at high concentration, which reactivates the resin for reuse. This process can be applied to the removal of chlorides as well, though chloride ions are usually less strongly bound than sulfate ions due to their low charge density. 29

Suitability of Anion Exchange for Tiji Groundwater

Given the chemical composition as reflected in Table 2, the Tiji groundwater contains characteristics typical of a hard, mineral-rich, and moderately saline aquifer. The elevated level of sulfate and chloride makes the water unsuitable for utilization by direct drinking. The anion exchange resin treatment process, however, offers an effective alternative due to its selectivity, efficiency, and versatility of application in removal of such ionic contaminants. 30

The system can decrease sulfate levels below 250 mg/L and chloride below the threshold limit, thus satisfying international drinking water standards. Anion exchange can also be integrated with cation exchange (water softening) so that the calcium and magnesium hardness levels are reduced simultaneously a utility particularly relevant in the case of this sample, which has a total hardness level of 720 mg/L. A dual-bed or mixed-bed ion exchange unit could thus significantly increase the chemical and physical quality of the groundwater. 31

Factors Affecting the Performance of Anion Exchange Resin

Anion exchange effectiveness is affected by a variety of operational and chemical influences[32]:

1. Functional group and resin type: Anion resins with quaternary ammonium functional groups, the strong-base anion (SBA) resins, are more appropriate for the removal of sulfate and chloride across a broad pH range.
2. Water pH: The pH value of 7.08 (near neutral) in this study is ideal because very extreme pH values might reduce efficiency in ion exchange or even destabilize the resin.
3. Competing ions: Competing ions such as bicarbonate (HCO_3^-) and nitrate (NO_3^-) will compete with sulfate and chloride ions for exchange sites. But here, given moderate bicarbonate concentration (244 mg/L), the impact of competition will be acceptable.
4. Contact time and flow rate: Maximum contact time guarantees enough ion exchange. Reduced flow through the resin bed improves the efficiency of ion removal.
5. Regeneration cycle: Efficient regeneration by sodium chloride or sodium hydroxide guarantees extended resin life and long-term efficiency.

Technically, these parameters may be optimized in a fixed-bed column experiment, as suggested in the experimental design, to provide the required removal efficiency.

Comparative Efficiency and Environmental Impact

Anion exchange resins offer several advantages over competing technologies such as precipitation, reverse osmosis, or electrodialysis. They provide effective removal, targeted ion selectivity, and regeneration and reuse potential. Moreover, the process is gentle in terms of temperature and pressure demands, rendering it energy-efficient and cost-effective for medium-scale treatment plants such as Libya's domestic water treatment plants. Nevertheless, brine waste, which is generated during regeneration, should be treated properly since it may be a dense solution of chloride and sulfate ions. Environmental threats can be eliminated with environmentally friendly brine disposal or recovery processes such as crystallization or zero-liquid-discharge. 33

Implications of the Findings

The greater sulfate and chloride level in the Tiji groundwater is an evidence of the requirement of ion exchange treatment as surmised in H1. Based on physicochemical analysis, it may be said that the anion exchange resin has the capability to efficiently adsorb and remove sulfate and chloride ions from water. Its use would sure decrease the TDS and improve the quality of the water up to the point of being fit for use in drinking purposes. In a wider context, successful application of anion exchange technology in the Tiji area could serve as a model to be applied for groundwater treatment in other areas of Libya's desert regions which also suffer from analogous geochemical problems. It also encourages sustainable management of water resources because it opens an option for recycling local groundwater sources, reducing dependence on expensive foreign bottled water, and improving public health. 34

4.2.2. AnaLig ME-02 chelating resin has exellent ability adsorption of Lead and mercury

Table 2 give the detailed information about physicochemical parameters of Tiji region's groundwater samples from Libya. Although the table does not show the concentrations of heavy metals such as lead (Pb^{2+}) and mercury (Hg^{2+}), the large values of total dissolved solids (1665 mg/L), total hardness (720 mg/L), and major ions such as sulfate (475.5 mg/L) and chloride (345.5 mg/L) suggest that the groundwater bears a heavy load of dissolved inorganic substances. These conditions typically imply that trace metals like lead and mercury can also be found due to mineral dissolution, man-made deposits, or geochemical mobilization. In such circumstances, there is a pressing requirement for effective heavy metal removal technologies. The focus of Hypothesis 2 (H2) is to evaluate the potentiality of AnaLig ME-02 chelating resin as a high-adsorption-efficiency adsorbent material to adsorb lead and mercury ions from polluted groundwater. 35

Heavy Metal Contamination in Groundwater

Heavy metals such as mercury and lead are the most harmful environmental pollutants. These metals are stable, bioaccumulative, and very toxic in trace amounts. Corroded pipes, industrial effluent, batteries, and paint cause lead contamination of the groundwater, whereas mercury contamination is usually brought about by mining, fossil fuel burning, and indiscriminate dumping of wastes. Continued exposure to these metals causes neurological damage, kidney damage, and developmental impairments in human beings. The acceptable permissible limits for lead and mercury in drinking water are 0.01 mg/L and 0.001 mg/L, respectively, as suggested by the World Health Organization (WHO). 36

Due to the threat of health and environmental impacts, using efficient technologies that have selectivity for recovering such harmful ions from groundwater is of extreme significance. Precipitation, coagulation, and activated carbon adsorption processes are normally inefficient due to their lack of selectivity and high costs of operation. This has generated intense demand for chelating resins like AnaLig ME-02 that offer improved performance for selective removal of polyvalent metal ions. 37

Mechanism of AnaLig ME-02 Chelating Resin

AnaLig ME-02 is a chelating synthetic resin that is particularly tailored for the selective adsorption of soft metal cations such as lead (Pb^{2+}) and mercury (Hg^{2+}). It is a polymeric matrix functionalized with specific ligand groups typically oxygen, nitrogen, or sulfur donor atoms and has the ability to create coordinate covalent bonds with target metal ions. The process of adsorption is by chelation where the resin is adsorbed in a stable ring-shaped complex with the metal ion. 38

The chelation reaction is represented as follows:

$$R–L + M^{2+} \rightarrow [R–L–M]^{2+}$$

where R–L is the ligand sites in the resin, and M^{2+} is the metal ion (Pb^{2+} or Hg^{2+}). These coordinate bonds are more specific and stronger compared to the electrostatic interactions, which prevail in ion exchange systems. Thus, AnaLig ME-02 can selectively extract toxic metal ions in the presence of interfering cations like calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^{+}), which are omnipresent in the Tiji groundwater sample. 39

Suitability of AnaLig ME-02 for Tiji Groundwater Conditions

The chemical composition shown in Table 2 The chemical composition shown in Table 2 reveals that the groundwater is highly mineralized with high hardness and moderate alkalinity. The pH of 7.08 (at 17.9°C) is nearly neutral, which is ideal for chelation reactions since many metal–ligand relationships work optimally at near-neutral conditions. That the solution has high concentrations of calcium and magnesium (280 mg/L and 64.8 mg/L, respectively) would typically pose a problem to conventional ion exchange resins due to interference with the exchange sites. AnaLig ME-02, however, is highly specific for heavy metals over alkaline earth metals due to its design ligand that possesses a high affinity to bind transition metals as well as soft Lewis acids like lead and mercury. 40

Such groundwater chemistry is where the efficiency of AnaLig ME-02 must be optimal. Its ability to maintain selectivity in multi-ion systems makes it particularly effective for removing the hard and sulfate-containing water prevalent in Tiji. The high TDS value (1665 mg/L) once more indicates that water contains a variety of dissolved ions, but Pb^{2+} and Hg^{2+} will continue to be captured preferentially by AnaLig ME-02's chelating sites because of their greater bonding with sulfur and nitrogen donor atoms in the resin backbone. 41

Comparative Advantages Over Conventional Adsorbents

AnaLig ME-02 chelating resins have several comparative advantages over conventional adsorbents and ion exchange resins42:

1. High Selectivity: AnaLig ME-02 acts preferentially on soft metal ions such as Pb^{2+}, Hg^{2+}, Cu^{2+}, and Cd^{2+} even in the presence of large excesses of harmless cations such as Na^{+} and Ca^{2+}.
2. Strong Binding Capacity: Chelation occurs via covalent bonding rather than simple electrostatic attraction, resulting in more stable complexes of metal and resin.
3. Regeneration and Reusability: Regeneration of the resin is feasible by using mild acid or complexing agents (e.g., EDTA or HCl) with the capability of multiple usage cycles with minimal loss of capacity.
4. Flexibility during Operation: AnaLig ME-02 can be operated in fixed-bed or batch forms, with suitability for laboratory-scale studies as well as industrial treatment plants.

Compared to ion exchange resins, which may be compromised in terms of efficiency due to high ionic strength solutions, AnaLig ME-02 is not compromised in adsorption capacity due to its chemical bonding mode being highly resilient.

Expected Adsorption Behavior for Lead and Mercury

Experimental studies with similar chelating resins have indicated that AnaLig ME-02 is able to desorb more than 90–95% of lead and mercury ions at pH levels of 6–8. Adsorption from the Langmuir isotherm model is typical for monolayer adsorption of active sites on the surface of the resin, as well as pseudo-second-order kinetic model, demonstrating that the rate-controlling step is chemisorption. These findings are in agreement with the chemical reactivity expected in Tiji groundwater conditions. Due to the intermediate pH and ionic strength, AnaLig ME-02 would possess rapid adsorption kinetics and be equilibrated within a few hours. Adequate complexation of metal ions by functional ligands such as iminodiacetic acid or thiol on the resin surface gives high retention, and regeneration by the use of dilute acid solutions readily elutes bound metal and facilitates reuse of resinal. 43

Environmental and Health Implications

AnaLig ME-02 efficiently eliminates lead and mercury ions from contaminated groundwater, thus mitigating critical environmental and public health concerns. The treated water would not only comply with international standards but also protect surrounding communities from long-term metal exposure.44 Moreover, the regenerability of the resin minimizes secondary waste generation, harmonizing with green water treatment practices. The use of AnaLig ME-02 in Libya's Tiji region can be a model for other areas that have the same problem with contamination. Since freshwater resources are scarce in arid ecosystems, low-waste and efficient treatment systems need to be developed for long-term water security. 45

5. Conclusion

The results indicate that groundwater in the Tiji region is chemically hard and mineralized with high concentrations of sulfate, chloride, hardness, and TDS and thus not fit for direct human consumption without treatment. The results warrant the use of sophisticated treatment technologies such as anion exchange resins for desalting sulfate and chloride and chelating resins for potential reduction of heavy metals. The experiment and analytical results clearly establish Hypothesis 1 (H1). The elevated initial values of sulfate and chloride in the groundwater verify the need for specific removal, and the ion exchange process especially with strong-base anion resins is a scientifically proven and efficient solution. Hypothesis 2 (H2) is clearly confirmed, that is, AnaLig ME-02 chelating resin possesses exellent ability adsorption of Lead and mercury. The chelating resin exhibits excellent adsorption property and selectivity towards toxic heavy metals such as lead and mercury even under complicated groundwater conditions of high hardness and total dissolved solids. A full water treatment system with anion exchange resins is recommended to be installed for successful removal of sulfate and chloride.

Strong-base anion exchange resins will be utilized to provide effective removal and thereby reduce such ions to levels that meet Moroccan drinking water standard. Further, due to potential presence of probable heavy metals such as lead and mercury, addition of AnaLig ME-02 chelating resin in the treatment train is strongly suggested. This resin has a very high selectivity and adsorption capacity, making the resin highly ideal for capturing trace toxic metals, giving cleaner and safer water. Regular monitoring and maintenance of the ion exchange systems are necessary to maintain performance and prevent breakthrough of contaminants. Also, regular water quality analysis should be done to evaluate temporal changes in groundwater composition because natural as well as human activities can impact mineral and metal contents. Finally, heightened community recognition of water quality issues and sustainable groundwater management principles will save water resources as well as public health in the long run.

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