HEAVY METALS REMOVAL USING NATURAL ZEOLITE ADSORPTION FROM TIGRIS RIVER WATER AT SAMARRA CITY (IRAQ)

Purpose. The current study was conducted to evaluate the heavy metals adsorption and sorption rate when removing them from water and processing it in the Tigris River in Samarra city, Salah El-Deen, Iraq in 2021–2022 and evaluate the efficiency of zeolite for removing heavy metals, as well as to determine the high and low adsorption percentage from all heavy metals found in the river.

Methodology. The study included the analysis and measurement of physical and chemical properties with low-cost natural processing with no side effects to reduce the heavy metal in the Tigris River.

Finding. The results of the present study showed that the conductivity and turbidity of water decreased from 1596 to 727 µS/cm, from 343 to 22 naphthalene unit (NTU), respectively, and turbidity decreased from 633 to 491 ml/L. The concentrations of biological dissolved oxygen, total suspended solid, and total dissolved solid increased, while those of preprocessing nitrates (12.2 mg/l) differed significantly from the results of post processing (52 mg/l). Repetitive measurements showed good results for heavy metals such as Cr\(^{2+}\), Cd\(^{2+}\), Cu\(^{2+}\), Pb\(^{2+}\), Zn\(^{2+}\), Ni\(^{2+}\) and Co\(^{2+}\) with 16.3, 23.1, 6.3, 14.4, 8.1, 12.5 and 17.4 mg/l, respectively; the adsorption percentage was 81.6, 81.5, 86.7, 87.3, 76.4, 89.5 and 79.7 %, respectively.

Originality. The work showed the efficient processing of sewage water when treated with zeolite rocks powder being low cost and easy to use to adsorb heavy metals from water.

Practical value. Zeolite as a powder ground in different sizes could be used as a layer in the filter that purifies the water to become a drinking water with low heavy metal concentrations as well as with some other factors.

Keywords: heavy metals, natural zeolite, adsorption, sorption

Introduction. Drinking water contamination by heavy metals such as Chromium, Cadmium, Coppers, Lead, Zinc, Nickel, and Cobalt is a widespread phenomenon. Heavy metals are a major concern in this phenomenon because of their nature featuring toxicity, bio-accumulative and persistence. This kind of water pollution could cause serious hazards for human health and food chain, which has led to harm to the biological environment [1].

In recent years, heavy metals river pollution has been taking a place in many countries because the concentration is higher than the recommended guidelines issued by the World Health Organization (WHO) [2].

Methods for treating water in past decades which were offered to purify river water were various such as Flootation, Adsorption, Phytoremnediation, Membrane Filtration, Electro-chemical Treatment and Chemical Precipitation. The widely used method is “Adsorption”. This method is low cost and eco-friendly in treating polluted water by using Adsorbents Anions to remove heavy metals cations including resins for iron exchange [3].

Often, zeolite is chosen because of the porous structures and high adsorption capacity with low price. As adsorbent stone, zeolite is interesting and expected to have the best capacity adsorption.

During past years, employment of zeolite as absorbent and remover of heavy metals with different concentrations has been increased [4].

There are around 40 different forms of natural zeolite in the world. Clinoptilolite, mordenite, philippsite, chabazite, stilbite, analcime, and laumontite are common forms; offretite, paulingite, barrerite, and mazzite are uncommon forms. Clinoptilolite is the most prevalent natural zeolite among these and is utilized extensively around the globe. Zeolites have a three-dimensional structure called HEU and are made up of (Si, Al)\(_2\)O\(_4\) tetrahedra connected at all of their oxygen vertices. These channels allow for the exchange of cations and H\(_2\)O molecules, which balance out the negative charge left over from the isomorphous substitution. A negative charge is created in the lattice when Si\(_4\) is replaced by Al\(_4\), which is balanced by the exchangeable cation (sodium, potassium, or calcium), and is then replaced with heavy metals. K, Na, and Ca can be found in the composition with aluminum ions as small molecules large enough to occupy the position in the center of the tetrahedron of four oxygen atoms. Zeolites have the typical chemical formula M\(_{1/2}\)/n [Al(Si, O\(_2\))\(_4\)\(_x\)\(_y\)\(_z\)\(_w\)] \cdot PH\(_2\)O, where n is cation charge, y/x = 1−6 and x/y = 1−4, and M is (Na, K, Li), and/or (Ca, Mg, Ba, Sr) [5].

Because it is readily available and inexpensive, natural zeolite is particularly appealing for a variety of uses. Adsorption efficiency and cation exchange capacity depend on the zeolite’s chemical and structural makeup, specifically its Si/Al ratio, cation type, number, and location. These characteristics can be altered chemically to improve the material’s hydrophilicity or hydrophobicity for various ion or organic adsorption [6].

Simple acid/base treatment and surfactant modification were the main ways used to modify zeolite. The contaminant that obstructs the pores can be removed using simple acid
washing, which increases the rate at which cations are removed from wastewater because larger and more cations can enter pores as a result of the pores’ increased size. Ion exchange with \( \text{H}^+ \) has a significant impact on the micro-porosity and specific surface area of zeolites, according to certain studies on natural zeolites from various regions treated with HCl solution [7].

The H-form zeolite has a high capacity for exchanging metal ions. Utilizing organic surfactants to alter the surface property of zeolites is another means of modifying them, which can increase the range of applications for them in wastewater treatment. According to Misaelides (2011), quaternary amines, which may sorb anionic species and nonpolar organics [8, 9], produce a bilayer-like structure on the surface of zeolites and are the most often utilized modifying agents.

Surfactant modification zeolite can not only sorb anionic species but also exchange with metal cations because the cation size of modifying agents is too large to enter the inner channel and will not affect the chemical structure of zeolite [10].

Application for heavy metals removal. Heavy metals are often classified as metals with a density of > 5 g/cm³. There are many elements that fit into this group, but Cd, Cr, Cu, Ni, Zn, Pb and Hg are the ones that matter in the context of the environment [11].

Health risks from heavy metals include stunted growth and development, cancer, organ and nervous system damage, and in severe cases, death. Different sectors produce heavy metal-filled industrial effluents. Chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition are some common methods for removing heavy metals.

Natural zeolites are of tremendous interest as a heavy metal adsorbent because of their valuable ion-exchange activity [12]. Different emissions containing heavy metals are increasing day after day. Methods with effective results have been developed to remediate effluents. To treat waste water or polluted water, the adsorption is a low cost-effective method to be used for reducing heavy metals. In the last two decades, natural and modified Zeolites were used effectively to reduce pollutants and heavy metals in water and water. The usage has extended to remove heavy metals from polluted solutions [13].

The mechanism of removing heavy metals is ion-exchange with main advantages such as selective and less sludge production, as well as meeting strict standard of discharge of ions from solution.

Usually, the process of heavy metals adsorption goes through three stages: first, adsorption on the surface; second, inversion; third, moderate adsorption inside microcrystal [14]. The most common metals (Pb, Ni, Cd and Cu) have been studied by erionite and clinoptilolite (CL) (ER). Because of its specific surface area, ER has a greater propensity to absorb cations. The specific surface of CL is lower, which means there will be less response.

The multi-ion systems that produced the results have different adsorption speeds [15].

Materials and methods. Sample collection. Zeolite powder was used in the test samples. Zeolite was taken from the “Hosseinia” district of the Al-Anbar governorate and ground into a fine powder in a laboratory electric grinder. The powder was then run through a sieve with 0.5 mm-diameter holes. After that, the powder was wrapped in plastic bags and stored there until needed.

How to use Hydrotherapy. Zeolite rock powder was employed in specific ratios (2, 4 and 8) per 100 ml of contaminated water. The best concentration was then chosen for the treatment.

Physical and chemical characteristics. Electrical conductivity (EC). The EC of the samples was measured using a multi-parameter analyzer (Lovibond, con200 model), and the findings were represented in micro siemens (μS/cm). The following calibration with buffer solutions with a pH of 4, 7 and 9, a consort-type pH meter (C830) was employed. Biological Oxygen Demand (BOD) bottles were filled with a 250 ml sample, transported to the lab, and stored for five days in a water bath at 25 °C using the same technique for detecting dissolved oxygen, mg/l. Water turbidity was measured using a HANNA-LP2000 turbidity meter, which after being zeroed expresses standard solutions in nephelometric unit (NTU), the brownish unit. A 100 ml sample of the dissolved components was filtered using 0.45 μm filter paper, and the filtrate was collected in a jar with a given weight (B). The filtrate was then dried for 24 hours at a temperature between 103 and 105 (C) in an oven before being weighed (A). A 100 ml sample of the suspended solids was filtered using a 0.45 μm filter paper with a known weight to determine their concentration (B). The filtrate was then dried for 24 hours at a temperature of 103—105 in an oven [16]. The ultraviolet-visible Bio-chromic LKB Spectrophotometer was used to measure nitrate using the ultraviolet spectrophotometry screening method. Each sample’s absorbance was measured at 220 and 275 nm, and the nitrate concentration (mg/l) was calculated from each curve’s equation using standard solutions [17].

Selection a zeolite treatment. Zeolite is a wholly natural product that was produced millions of years ago as a result of geological processes like the breakdown of volcanic glass and its interaction with alkaline water [18]. With the chemical formula (K₂, Na₂, Ca₃)Al₆Si₃O₁₂·2H₂O, zeolite, commonly referred to as clinoptilolite, is mostly made up of SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O and TiO₂ as 70.00, 10.46, 0.46, 0.20, 2.86, 4.92, 0.02 and 1.2, respectively [19]. These natural ion exchangers, which have an alumino-silice molecular structure and weak positive bonding sites, are among the most well-liked and generally accessible ones [20]. A key component of the treatment process utilized to eliminate and lessen some physical and chemical elements that contribute to pollution is zeolite. In order to get the best possible treatment, zeolite was pulverized and applied to samples taken from the Tigris River’s water plants.

Heavy metals measurements. After adding the grinded powder of natural zeolite, the water from the Tigris River was added to the container. Then, the outcome water was collected and the heavy metals were determined using the Flame Atomic Adsorption. Results were recorded and are shown below.

Results and discussion. Table 1 shows the changes in the estimation of some physical and chemical characteristics for water of the Tigris River at Samarra city.

**pH**: Acidic, alkaline, or what is known as the hydrogen ion concentration in water, where the recommended pH levels in most drinking water range from 6.5 to 8.5 degrees.

Water that has a higher pH, that is alkaline, may cause digestive problems for some people, if the person has high acidity in the stomach. This could explain the increase in the popularity of alkaline water for drinking in the past period, which led to the development, cancer, organ and nervous system damage, and in severe cases, death. Different sectors produce heavy metal-filled industrial effluents. Chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition are some common methods for removing heavy metals.

Table 1: Physical and chemical characteristics for water of the Tigris River at Samarra city.

<table>
<thead>
<tr>
<th>Measurments of Tigris River in Samarra city</th>
<th>Allowed limits</th>
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<tbody>
<tr>
<td>pH</td>
<td>7.4</td>
</tr>
<tr>
<td>EC μS/cm</td>
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<tr>
<td>TSS mg/L</td>
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<td>TDS mg/L</td>
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<td>BOD₅ mg/L</td>
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<td>Turbidity NUT</td>
<td>273</td>
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<tr>
<td>Total Hardness mg/L</td>
<td>162</td>
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<tr>
<td>NO₃ mg/L</td>
<td>52</td>
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Table 1: Physical and chemical characteristics for water of the Tigris River at Samarra city.
leads to neutralizing the acids in the digestive system, and making the person feel more comfortable.

The study’s findings (Table 1) showed that there were considerable variations in the pH of the water taken directly from the river which was the subject of the investigation. The treatment had an impact on lowering pH, which was consistent with a zeolite efficiency study’s findings according to which, the greatest amount of pH could be removed with an efficiency of up to 85.95% [2].

**EC:** The EC stands for the positive and negative ions that were found in the water that was dumped from the study’s locations. The current study’s findings demonstrated that the discarded water from the several study sites varied in terms of EC in a highly significant manner (Table 1). The EC of the water emitted from Samarra water dam grew to 1586 μs/cm, while it dropped to 268 μs/cm in the liquefaction water. The effective operations at these locations caused various dissolved compounds in the water to leave departments, which is what caused the observed spike in EC. The degree of the solution grew as a result of the dissolved elements, which also enhanced the conductivity values. Regarding the impact of treatment methods, Table 1 study findings show that zeolite powder treatment may effectively lower these values, with EC reaching 719 and 164 μs/cm for water and liquefaction water, respectively [19].

**TDS:** One of the main elements of the water released by departments is total dissolved matter. They stand in for the wastes produced by operations, lab testing, or waiting rooms that used raw materials as a starting point. The values of TDS at the research site differ, as shown in Table 1. The water had the highest concentration of total soluble chemicals (957 mg/l), which was reduced to 354 mg/l after treatment. TDS levels in the liquefaction plant’s water sample were 178 mg/l. The abundance of wastes produced during and after operations, as well as during the cleaning of contaminated halls, may be the root of the high concentration of dissolved compounds. Table 1 displays how these materials were treated using various techniques [14]. The reduction of the content of total solids from the water treatment with zeolite powder was successful. After being exposed to zeolite powder, the concentration of these compounds dropped to 361 mg/l. The number of dissolved salts in the treated locations’ water was in agreement with earlier findings, and it is similar to the discovery made in [12].

**TSS:** The total suspended solids (TSS) in environmental research refers to the quantity of solid plankton in any water, including drinking water. Water becomes unsafe for human usage when there are excessive amounts of planktons present. Because formaldehyde is frequently used in pathological laboratory departments to preserve samples and sterilize medical equipment and tools, it is thought to be the most dangerous pollutant of water. This is the cause of the rise in TSS [5]. Therefore, detecting the concentration of these compounds and figuring out how to treat them to get rid of or lower their amount in water have been the focus of environmental study. Water treatment with zeolite powder demonstrated great efficacy in lowering the level of TSS in the water outside [8]. By using this drug, the TSS concentration was lowered from 0.48 to 0.06 mg/l. The Tigris River will become contaminated by zeolite chemical powder water treatment [20].

**BOD:** According to Table 1, the highest bio-oxygen concentration in the water was 101 mg/l, while the value following treatment was 48 mg/l. This increase in the need for oxygen may be brought on by the patients’ vital activities, which may also be the cause of the rise in organic excretions. An indication of the rise in BOD in the water that was leased [1]. The treatment with zeolite powder produced the best results in lowering BOD, according to the treatment parameters for water in Table 1. When liquefied water was treated, the concentration of vital oxygen demand was 11 mg/l higher than it was before processing [18]. The reason for this decline may be due to chemicals that can bind to biological oxygen, which led to a reduction in its concentration in the aqueous medium, or the rise in the proportion of solvents used in medical laboratories and the amount of highly toxic mercury used in medical waste that is flushed into sewage systems. The BOD values for the treated samples mirrored those of one study [19], but were different from those of another study [18].

**Total Hardness:** Hard water is water that has a high mineral content (in contrast to “soft water”). Hard water is formed when water is filtered or in touch through limestone and chalk sediments consisting mainly of calcium and magnesium carbonate, which increased the dissolved ions in the water leading to hardness.

The Tigris River water had the greatest overall hardness value (628 mg/l) (Table 1), but following treatment, it reduced to 491 mg/l. The type of chemicals injected into these fluids and utilized in surgical operations may be the cause of the rise in hardness. The water that has been added to the river is the cause [3]. This result is consistent with the findings of several studies that claimed the waters in Iraq had high overall hardness. The Iraqi Standard Criteria and the World Health Organization’s specifications state that after treatment, the water is fit for human consumption [19].

**Turbidity:** Due to the significant amounts of suspended materials present, which disperse and absorb light to cool the water, water appears exceedingly murky. The brownish levels are significantly reduced, as shown by the treatment processes for waste water. According to the findings in Table 1, zeolite powder greatly reduced the brownish value of water. The brownish value was 339 NTU prior to therapy, and it was lowered to 18 NTU following zeolite treatment. Zeolite powder’s ability to reduce brownish values is a result of its ability to trap plankton and elevate its molecular weights, which results in sedimentation at the bottom and improved water clarity. It also contains these properties. This powder is made up of limestone and limestone grains. The outcomes for the brownish values matched those of a study [19].

**Nitrate (NO₃⁻):** It should be observed very well because of nutritional enrichment (Eutrophication) when it is present with phosphorous in high concentrations, which stimulates and causes excessive growth of algae, affecting the food web in the water. The European Union directives regarding drinking water stipulate that the level of nitrate in one liter of water does not exceed 50 milligrams, a level that the European Union considers “safe” for the health of the consumer. There are fears that nitrates can be transformed by chemical processes into nitrites that causes several problems to human health.

Before using zeolite powder as a therapy, the nitrate level was 27.6 mg/l. This figure was considerably different from the outcome following the therapy (14 mg/l). The tests and analyses that were done, in which nitrogen was the predominant component, could be the cause of the high nitrate value in the water. This element becomes nitrate when it interacts with the dissolved oxygen in water. Nitrate concentration is impacted by zeolite chemical powder water treatment [20].

**Heavy metals.** Zeolites and heavy metals removal comparison. Heavy metal immobilization is a difficult procedure, and the type of adsorbents used affects how well the metals are removed. Over the past 20 years, numerous scholarly studies have been written about using natural and synthetic zeolites as adsorbent to remove heavy metals from natural or industrial water. The ratio of zeolite to wastewater (S/L) temperature, contact time, initial concentration of metal ions, and solution pH all affect the amount of metal that may be absorbed. Using various zeolites as adsorbents, the ideal adsorption test conditions for the major metal ions into Cr⁶⁺, Cd⁰, Cu²⁺, Pb²⁺, Zn²⁺, Ni²⁺ and Co²⁺ are summarized.

**Cr²⁺.** By natural Zeolite, the maximum adsorption of Cr²⁺ reached (71.9) mg/g as shown in Table 2; the sorption rate is
18.4 %, the zeolite adsorption efficiency is greatly increased due to the inter-spaces between zeolite particulate which allows removing heavy metals through chemical bonds [21].

The adsorption quantity of Cd\(^{2+}\) is (101.3) as shown in Table 2. The efficiency adsorption of Cd\(^{2+}\) ion content could be decreased when the ion content in solution is lower than 100 mg/l. Another study reported that synthetic zeolite sorption capacity for Cd\(^{2+}\) could be ten times greater than that of natural zeolite [22].

The Cu\(^{2+}\) can be adsorbed and removed by natural zeolite. The adsorption quantity as shown in Table 2 being 41 mg/g, as a comparative activated carbon as adsorbent could be very low because of chemical bonds with Na ions, is faster; also the natural zeolite treated with any compound contains Na such as NaCl and NaOH or even CH\(_3\)COONa. This modified zeolite has high rate of sorption and can be used to remove copper ion from low content water. The sorption value would be higher compared to natural zeolite when the condition of sorption is the same.

Pb\(^{2+}\) could react to different adsorbent material. The Pb intake capacity of natural zeolite could reach 98.4 mg/l at normal temperature. As another study showed, the temperature and pH may have role to increase the capacity of zeolite Pb intake. The structural diversity of natural zeolite is significant for Pb adsorption in the water. The modified zeolite is favorable to reduce Pb [24].

Zn\(^{2+}\) the natural zeolite can adsorb about 26.1 mg/l of Zn\(^{2+}\), the sorption rate of Zn value can be higher when the concentration is 100 mg/l or more [25].

Ni\(^{2+}\) Table 2 shows the adsorption rate of Ni\(^{2+}\) is 89.5 %; this rate is high because Ni\(^{2+}\) reacts with natural zeolite and this would be higher when water content is 500 mg/l at room temperature.

Cu\(^{2+}\) Natural zeolite was used for metal sorption of Co\(^{2+}\). In Table 2 Co\(^{2+}\) adsorption rate is 89.9 % [25].

Conclusions.
Natural Zeolite has high adsorbent ability for heavy metals. In particular, for Ni\(^{2+}\) and the lowest adsorbent ions it was Zn\(^{2+}\) in the main drinking water source of the Tigris River. More importantly, the heavy metals adsorption capacity is an efficient and low-cost method with good results.

The natural zeolites of “Hosseinia” region are promising sorbents for extracting heavy metal ions from aqueous solutions. It can work with different heavy metals concentrations from low to high.

References.
Вилучення за допомогою адсорбції природним цеолітом важких металів із води річки Тигр у місті Самарра (Ірак)

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Мета. Дане дослідження було проведено, щоб оцінити адсорбцію та швидкість сорбції важких металів, при витягуванні з води та її обробці, річки Тигр у місті Самарра, Салах Ель-Дін, Ірак у 2021—2022 роках, а також оцінити ефективність вилучення важких металів цеолітом, визначити високий і низький відсоток адсорбції всіх вивчених важких металів у воді даної річки.

Методика. Дослідження включало аналіз і вимірювання фізичних і хімічних властивостей за допомогою недорогої природної обробки без побічних ефектів з метою зниження вмісту важких металів у воді річки Тигр.

Результати. Результати цього дослідження показали, що провідність і каламутність води знизилися з 1596 до 727 мкСм/см, з 343 до 22 нафталінових одиниць (NTU) відповідно, а каламутність знизилася з 633 до 491 мл/л. Концентрації біологічного розчиненого кисню, загальної кількості завислих речовин і загальної кількості розчиненої твердої речовини збільшилися, а концентрації нітратів попередньої обробки (12,2 мг/л) значно відрізнялися від результатів постобробки (52 мг/л). Повторні виміри показали хороший результат для важких металів, таких як Cr3+, Cd2+, Cu2+, Pb2+, Zn2+, Ni2+ і Co2+: 16,3; 23,1; 6,3; 14,4; 8,1; 12,5 і 17,4 мг/л відповідно, відсоток адсорбції складає 81,6%; 81,5%; 86,7%; 87,3%; 76,44%; 89,5% та 79,7% відповідно.

Наукова новизна. У роботі показана ефективна обробка стічних вод із застосуванням подрібненого порошку цеоліту при низькій собівартості та простоті використання для адсорбції важких металів з води.

Практична значимість. Цеоліт у вигляді порошку, подрібненого до різного розміру, може бути використаний як шар у фільтрі, що очищає воду до стану питної води з низьким вмістом важких металів, а також з деякими іншими факторами.

Ключові слова: важкі метали, природний цеоліт, адсорбція, сорбція

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