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ORIGINAL RESEARCH ARTICLE

Physical treatment of wastewater in Ramadi Hospital using zeolite and natural sand

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ABSTRACT

Water quality is a huge challenge in Iraq due to insufficient modern infrastructure for the effective treatment of wastewater, which leads to the release of non-purified effluents into river ecosystems and increases the risks for human beings' health significantly. The purpose of this research is the evaluation of white sand and natural zeolite performance as environmentally friendly and energy-saving filtration materials in removing pollutants from hospital wastewater. Multi-layer filtration systems were designed to investigate the effectiveness of both materials independently, and then to conduct the study of the combined use of the Sand-Zeolite filter under different operating conditions (flow rate, hydraulic retention time, HRT).

The data obtained during the experiment prove that the combination of filtration materials improves their effectiveness in purifying wastewater from various pollutants. For instance, the efficiency of EC purification increased up to 89%, whereas TDS was removed on 69%. Moreover, the combined use of sand and zeolite demonstrated outstanding results in reducing organic load, and both BOD and COD decreased by 93% and 75%, respectively. The analysis showed that TBC was removed on 88%. Ammonia removal by the filter of the dual structure increased up to 99.6%, whereas individual use of filters resulted in the removal of ammonia by 99% (sand) and 99.7% (zeolite). It is also important to mention the efficiency of nitrate purification by Sand-Zeolite filter (64%), whereas the removal efficiency of nitrites was 56%. Sulfate (100%) and phosphorus (89%) were completely removed from wastewater by the tested filter. Heavy minerals' purification results indicated a complete removal of iron (Fe, 100%) and zinc (100%). As to chromium (87%), copper (86%) and nickel (51%) purification results, they can also be considered excellent.

Thus, the combination of the filtration properties of white sand and zeolite proves to be a sustainable approach to purifying wastewater. The proposed methodology allows creating high-quality reclaimed water. The technology is extremely promising and affordable.

Keywords: wastewater treatment, heavy minerals, natural zeolite, sand filtration, sustainable development, ammonia nitrogen removal, hospital effluent

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1. Introduction

Water pollution is one of the significant issues of the twenty-first century, negatively affecting the environment, people, and other organisms[1,2]. The reasons behind the issue include rapid population growth, industrial development, climate change, and poor availability of drinking water. One of the priorities among the Sustainable Development Goals is clean water and sanitation that should be achieved until 2030[3].

Hospital effluent water contains many hazardous substances such as pathogenic microorganisms, partly metabolized medicines, radioisotopes, and various toxins like antineoplastic agents, antibiotics, and organ halogens. These pollutants are often not eliminated in regular WWTP facilities; therefore, they can affect the biological balance of receiving environments. Consequently, primary water treatment of hospital sewage before discharging it into municipal sewers becomes critical[4].

There were numerous attempts to create new methods of wastewater purification through various processes including biodegradation, filtration, ion-exchange, and membrane filtration. Hybrid systems can also be used to improve treatment efficiency[5,6]. Sand filters are advantageous because of their simplicity, low maintenance, and negligible use of chemicals, energy, and area in comparison with other natural systems. Efficiency of the system relies on high hydraulic loading rate and is connected with the sand layer thickness. Big size of sand grains contributes to the development of a thick biofilm layer and increases biological activity which creates the necessary environment for biodegradation or mineralization of pollutants[7].

Natural zeolites are microporous crystalline aluminosilicates possessing well-ordered framework structure. These materials have become widely used in petrochemical, chemical, and water industries thanks to their ion-exchange capacity, accessibility, and low cost[8,9]. Natural zeolites usually are formed as a result of hydrothermal processing of volcanic ashes at certain temperatures and pressures[10]. Unusual properties make them suitable for different uses in catalysis, ion-exchange processes for heavy metal and radionuclides extraction, gas separation, and adsorption operations[11,12].

Activated carbon is considered to be one of the most effective absorbers of pharmaceuticals and organic molecules. At the same time, it cannot compete in removing ammonia and heavy metals[13]. Likewise, although bentonite successfully removes dyes, it does not have ion-exchange capabilities comparable with those of zeolites. On the other hand, sand filtration mainly operates based on the straining effect. As a consequence, zeolites become very effective adsorbents of water contaminated with metals and organic compounds and CO2.

2. Significance and Objectives of the Study

2.1. Research Significance

However, lack of efficient treatment of hospital wastewater is one of the major environmental issues that need to be addressed in Ramadi. Significance of the investigation is determined by creation of a combined system, bridging the gap between efficiency of purification and financial considerations. As it uses naturally available zeolite and sand, as opposed to expensive activated carbon or chemical agents, this research facilitates implementation of Green Technology.

In terms of strategy, the objective is to convert contaminated water into a valuable source of water, suitable for limited agricultural or industrial use. The focus is not only shifted from traditional filtering methods to advanced cost-efficient chemical purification methods but also from easy to remove compounds to pollutants, which are difficult-to-remove compounds such as ammonia and heavy metals (lead, copper), due to their ion exchange property of zeolite.

2.2. Research Objectives

The primary objectives of this study are as follows:

1. Enhancing Filtration Efficacy: For determining the synergy between sand filtration, known for its ability to filter suspended particles, and zeolite, having better ion exchange properties, thus creating a combined physical and chemical water treatment method.
2. Improving Effluent Quality: In order to make sure that the wastewater meets the set standards to enable its reused in agriculture or industry and not be discarded.

3. Optimizing Disinfection Processes: In order to decrease the amount of organic matter and microorganisms before the initiation of the disinfection process (for example, chlorination and UV radiation), thus increasing the water quality.

4. Environmental Safety: To mitigate the risks associated with hazardous effluents before discharge or reuse.

5. Engineering a Sustainable System: To construct a highly efficient yet simple-to-maintain filtration system designed explicitly for the intricate nature of hospital wastewater.

3. Materials and Methods

3.1. Study Site and Experimental Framework

This experiment was carried out at the Experimental Station at the Upper Euphrates Basin Advisory Centre (UEBAC) for Research on Sustainable Development, University of Anbar. The aim was to investigate the efficiency of sand and zeolite in the treatment of raw wastewater by using a pilot system that resembles real conditions in the working process of industrial-scale sand filtration.

The source of the raw effluent was Ramadi Teaching Hospital for Maternity and Children, an important medical center in Ramadi. It consists of 11 ward rooms, 3 pharmacies, and one laboratory unit. In addition, an average of 20,432 patients receive outpatient services in this hospital, and 41,145 people receive inpatient services. The wastewater treatment plant (WWTP) operates at a design capacity of 350 m^3/h, and its technology involves three main stages: physical purification, aeration, and filtration, ending with a UV disinfection stage of 6 hours duration.

3.2. Environmental Implications

Presently, the effluents from the treatments are released into the Al-Warrar Regulator. The Al-Warrar Regulator used to receive water discharges when there was high river discharge from the Euphrates River. Nevertheless, drought has led to a reduction in these water discharges into the Al-Warrar Regulator. This makes the hospital’s waste effluent end up being discharged to Lake Habbaniyah, posing a great threat to the environment.

3.3. Sampling Protocol

Wastewater samples were obtained directly from the influent pump station in the collection and sedimentation chamber of the WWTP at the hospital facility. Composite sampling was done during a period of three months with three sampling sessions in each month.

• Temporal Scaling: The samples were collected at the busiest times of day (08:00 – 12:00), with sub-samples collected hourly until the complete sample was formed.

• Volume and Storage: The total volume that was collected for each event was 30 liters. The samples were placed in sterilized and clean high-density polyethylene (HDPE) bottles and then immediately conveyed to the laboratory for analysis.

• Comparative Assessment: Furthermore, samples of the treated wastewater from the hospital after WWTP treatment were collected according to the same strict sampling methodology to determine a benchmark for assessing the efficiency of the suggested system.

3.4. Analytical Methods and Laboratory Techniques

The water samples were subjected to various physico-chemical and microbiological analyses following the standardized techniques. The total dissolved solids and heavy metals like Ni, Cu, Fe, Cr, and Zn were estimated following the methodologies mentioned in sources[15,20]. Electrical Conductivity was measured using a Hanna EC meter. Concentrations of nitrite and nitrate ions were determined using a Hi83200 Multipara meter Photometer and expressed in mg/L concentration[16].

Sulfate ions and biological oxygen demand were determined using the techniques mentioned in[17]. Chemical Oxygen Demand was calculated by using a Lovibond MD200/COD VAR10 instrument. Other ions like K, NH4, and CaCO3 were estimated to be using the Hi83200 Multipara meter Photometer[18]. For bacteriological analysis, Total Bacterial Count was performed following the protocol given in[19].

3.5. Environmental Implications

Hospital effluent treatment was carried out using a locally constructed batch reactor facility. This unit included two upright glass tubes that were 130 cm long and had an internal diameter of 10 cm.

• Column 1 (Single-Media Sand Filter): The sample included white sand that washed four times using distilled water prior to use, to remove any foreign particles and clay. The effective size of the sand particles used was 0.2 – 1 mm, which gave rise to a 25-cm thick bed of sand. Below the bed, there was a 2-cm support layer made up of graded gravel particles (1 – 3 mm).

• Column 2 (Zeolite Filter): The design included a natural zeolite medium, which was 25 cm thick, resting on a 2-cm-thick layer of gravel. To avoid mixing the media layers, a thin sieve was placed in between the two media layers, while a screen at the bottom ensured that the medium was not lost and that the drainage layer was not clogged.

3.6. Operational Procedure and Treatment Stages

The columns were fed with raw hospital sewage that was kept in a main tank. A digitally programmed pump regulated the flow of the feed water at a hydraulic loading rate of 30 L/m2/day. The feeding was done intermittently, whereby about four liters of sewage was introduced into the columns every two hours. The treatment process involved three phases:

1. Stage I (Sand Filtration): Aeration of the wastewater was done 30 minutes before introducing it into the columns. The filtrates were taken after a 20-minute interaction time.
2. Stage II (Zeolite Filtration): In another similar experiment, the water was subjected to aeration process for 30 minutes followed by filtration using the second filter. A fraction of the samples was collected with 20 minutes of retention time.
3. Stage III (Hybrid/Dual-Media System): The discharge from Column 1 (sand) was transferred straight to Column 2 (zeolite). After a retention time of 20 minutes in Column 2, the treated water was then analyzed thoroughly. **Figure 1** shows the components of the laboratory batch reactor and the sequence of treatment stages, including the distribution of the sand and zeolite filter columns.

All statistical tests were carried out using the software package Minitab(r) version 19 (Minitab Inc., State College, PA, USA). Descriptive statistics (means and standard deviation) were calculated for all parameters at each sampling point. The statistical comparison of differences among treatments was made by applying one-way analysis of variance (ANOVA), with the aim of comparing West water, Sand filter, Zeolite filter, and Sand & Zeolite filter stages. The HSD test was used for post hoc comparisons. Correlation analysis was performed where appropriate. Statistical significance was considered at the levels of $\alpha = 0.05$ ($p < 0.05$) and $\alpha = 0.01$ ($p < 0.01$). The removal efficiency was computed as follows: $RE = [(C_0 - C_t) / C_0] \times 100$, where C_0 is the initial concentration and C_t is the final concentration.

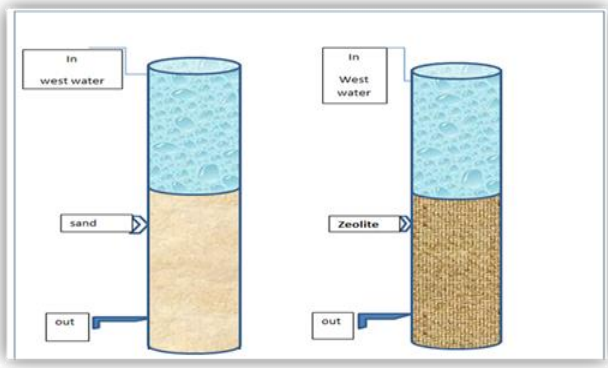

Figure 1. Components of the laboratory batch reactor and the sequence of treatment stages, including the distribution of sand and zeolite filter columns.

4. Results and Discussion

4.1. Baseline Characteristics of Treated Hospital Effluent

The physical and chemical characteristics of the treated wastewater from the existing hospital WWTP are presented in **Table 1** below. The analysis reveals that there is a considerable load of pollutants, which varies from moderate to high in several water quality parameters. While the existing WWTP can filter out some of the pollutants compared to the untreated influent, the treated wastewater does not meet both Iraqi and international environmental regulations.

The average levels of the EC and TDS were 335.00 ± 87.51 μS/cm and 1650.67 ± 415.19 mg/L, respectively. The high values show that the wastewater contains a significant level of dissolved ions and salts originating from different sources like organic matter, microorganisms, and inorganic substances. Moreover, the nutrient content was highly enriched by phosphorus (PO4-P), with 44.78 ± 21.26 mg/L and sulfates (SO4), with 134.00 ± 22.34 mg/L.

There were nutrients found in the sample in the forms of nitrate nitrogen (NO3-N) and nitrite nitrogen (NO2-N), with 2.33 ± 0.59 mg/L and 27.83 ± 0.83 mg/L, respectively. The high nutrient content is consistent with the high presence of organic matter in terms of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of 286.00 ± 180.60 mg/L and 233.00 ± 90.83 mg/L, respectively. The microbiological tests confirmed the presence of total bacterial count (TBC), which reached 4.77 × 10^6 ± 1.08 CFU/100 ml. Such nutrients and pathogens can persist in hospital wastewater due to human waste products, excessive use of cleaning materials, and pharmaceutical residues.

Table 1. Characteristics of treated wastewater at the hospital station (N=3).

Parameter	Unit	mean±SD
EC	ms/cm	335.00 ± 87.51
T.D.S	mg/l	1650.67 ± 415.19
BOD	mg/l	233.00 ± 90.83
COD	mg/l	286.00 ± 180.60
T.B.C	Cfu/100ml*10^6	4.77 × 10^6 ± 1.08
SO4	mg/l	134.00 ± 22.34
PO4	mg/l	44.78 ± 21.26
NH3	mg/l	2.7133±0.8279
NO2-N	mg/l	27.83 ± 0.83
NO3-N	mg/l	2.33 ± 0.59
NI	mg/l	0.41 ± 0.00
Zn	mg/l	0.36 ± 0.00
Cu	mg/l	0.53 ± 0.00
Fe	mg/l	1.3733±0.020

Cr	mg/l	2.0133±0.020
Chlorine	mg/l	2.4667±0 .001

*. The difference is also statistically significant at the 0.05 level

4.2. Analysis of EC and TDS Removal Efficiency

The experimental data obtained and presented in **Table 2** reveal the superiority of the hybrid filter (sand zeolite) and zeolite column filtration in terms of their efficiency to eliminate EC and TDS from the water sample compared to the traditional filtration through sand. Specifically, there was an evident discrepancy between sand and zeolite's performances, as the average EC of the influent decreased from 3491.3±2.3 µS/cm to 416.0±19.6 µS/cm when the water passed through the zeolite filter. Furthermore, the maximum EC elimination was reached when the hybrid filtration system (sand+zeolite) was applied, with the average EC level falling down to 374.3±26.5 µS/cm. Additionally, the proposed dual-media system showed excellent TDS elimination properties, with the average level equaling 703.33±15.50 mg/L. As can be seen in **Figure 2**, the dual-media system (S+Z) reached the maximum elimination rate of 89% for EC and 69% for TDS, seconded by the single zeolite filter (88% for EC and 69% for TDS). On the contrary, the contribution of sand in the process was limited solely to capturing suspended particles, having minimal effect on ionic composition, with the removal rate of EC and TDS equaling 54% and 19%, respectively.

When comparing the performance of the laboratory-scale prototype with the current treatment plant at the hospital (H.T.W.), where the average removal rate reached 90% and 27% for EC and TDS, respectively, one can notice significant advantages offered by the latter. Specifically, the enhanced effectiveness of the proposed prototype is related to its dual-mode operation, combining ion exchange and chemical adsorption processes, characteristic of natural zeolite, as described in reference[23]. The microporous crystalline structure of zeolite ensures efficient ion capture, decreasing the concentration of free ions in the solution, thus achieving a marked reduction in EC compared to sand filtration systems.

Additionally, there are several benefits associated with using zeolite compared to sand, including higher porosity and lower bulk density, thus requiring less material for treatment[24]. Another advantage lies in the unique ability of zeolite to provide ion exchange, ensuring the removal of pollutants that are resistant to sand filtration[24]. The results of this study coincide with those discussed in reference[25], highlighting the synergic effect of hybrid filters. The physical retention of solid particles by sand prevents clogging of zeolite active sites and maintains the efficiency of the ion-exchange process.

Table 2. Removal efficiency of different pollutants across various filtration media.

parameter	**West water**	**Sand filter**	**zeolite filter**	**Sand& zeolite filter**		
	Mean± St Dev.	Mean± St Dev.	Mean ± St Dev.	F-Value	P-Value	Mean± St Dev
EC µc/cm	3491.3 a± 2.31	1610.0 b ± 8.54	416.0 c ± 19.6	374.3 d ± 26.5	654.45	<0.000003**
T.D.S mg/l	2270 a ± 0.398	1847 b ± 0.0950	801.000 c ± 1.000	703.330 c±15.50	9398.43	<0.000006**
BOD mg/l	3567.00 a ± 53.2	320.00 b ± 10.0	151.33 c ± 3.21	151.00 c± 8.54	5.29	<0.027*
COD mg/l	575.70 a ± 31.1	271.00 b ± 7.94	169.33 c±0.577	146.33 c±3.51	45.50	< 0.0009**
T.B.C *10^6 Cfu/100ml	32.600 ± 1.000	8.600 b ± 0.200	5.167 c ± 0.153	4.000 d± 1.054	1003.46	< 0.000004**

Note: Different superscript letters (a, b, c) indicate statistically significant differences treatment stages according to Tukey's HSD post-hoc test ($p < 0.05$). ** indicates $p < 0.00$.

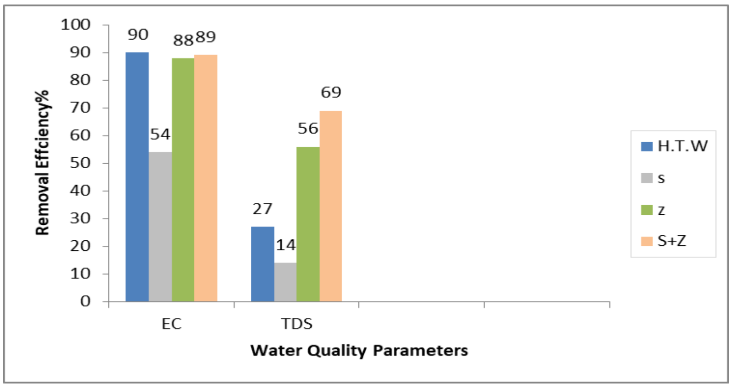

Figure 2. Evaluation of efficiency of removal of EC and TDS using three filtration setups: sole sand, sole zeolite, and a composite filtration setup using both sand and zeolite together.

4.3. Organic Matter Removal (BOD and COD Analysis)

As shown in **Table 2**, the results revealed that there was a significant decrease in BOD concentration. Most effective were the zeolite and the hybrid S+Z filters whose effluent contained the minimal concentrations, 151.33 ± 3.21 mg/L compared to the highly contaminated raw influent.

The above effectiveness mainly contributed to the fact that both sand and zeolite are used not only as bio-filters but also physical filters. Sand is first applied as an effective barrier filtering out suspended particles. On the other hand, the large specific surface area and the presence of microporous channels on zeolites provide good support for the development of microorganisms forming a biofilm layer, and hence supporting the aerobic oxidation of dissolved organics into stable metabolites thus reducing the BOD concentration[26]. This was made possible by the effectiveness of zeolite as a bio-carrier with 93% of efficiency in BOD removal as shown in **Table 2**. Additionally, the sand filter recorded a very high efficiency of 91% in removing the dissolved organics, implying a very strong biological activity involved in the process[25].

In the case of COD removal, there was significant difference ($p<0.05$) across the different stages. The hybrid system (S+Z) showed highest removal efficiency of 75% as well as the standalone zeolite with 71% while the hospital existing treatment system managed to remove 50%. As noted in[28], zeolite not only physically traps complex organic compounds based on their size and shape but also functions as a molecular sieve entrapping the complex organic compounds. Therefore, due to its ion-exchange nature and Van der Waals force, zeolite effectively mitigates complex organic loads. The hybrid S+Z was able to act simultaneously as a biological reactor as well as physical-chemical filtration system providing an additional barrier against complex pollution.

Finally, in relation to microbiological improvement, the hybrid system (S+Z) achieved the highest reduction of Total Bacteria Count (TBC) from the raw effluent of 32.600 ± 1.000 × 106 CFU/100 ml down to 4.000 ± 1.054 × 106 CFU/100 ml. According to the experiments carried out, the purification efficiency in the removal of both bacteria and organics was 88% and 84% respectively for S+Z and zeolite alone, while for the existing system was 85% (refer **Figure 3** below).

It is important to note that the high efficiency of the hybrid S+Z for the bacterial removal was mainly due to multi-level filtration. Specifically, through the use of sand layer, larger bacterial particles can be filtered preventing the blockage of active sites as well as masking effect and, hence, enabling zeolite to utilize its large specific surface area and electrostatic attraction to effectively trap fine bacteria. The above findings agree with[29] who suggested that the combination of sand and zeolite provides a complex environment increasing chances of bacteria contacting with the zeolite surface thus promoting physical disinfection without use of any chemical agents. In addition, beyond physical trapping, zeolites have antimicrobial properties. As stated in[30], zeolites may trap some metal ions including copper and zinc that oxidize trapped bacteria cells. These findings agree with[31] who showed removal efficiency of 50 – 67% COD with 90% bacteria removal when using sand filters (0.31 – 0.56 mm).

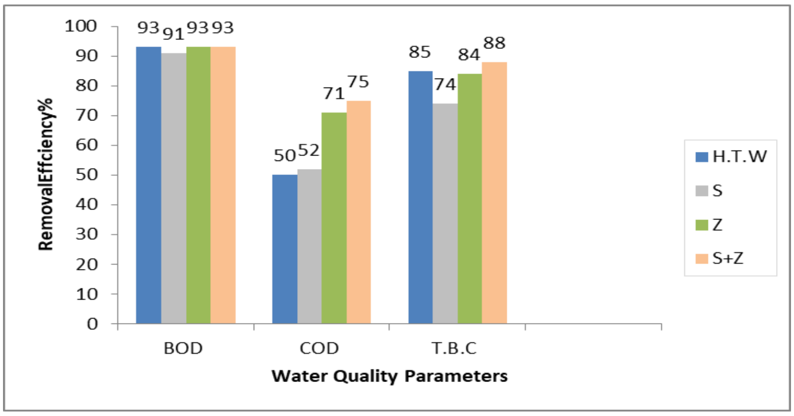

Figure 3. Comparison of removal efficiencies for organic pollutants (BOD, COD) and total bacterial count (TBC) across single-media (sand, zeolite) and dual-media (sand/zeolite) filtration systems.

4.4. Nutrient Removal Efficiency (Nitrogenous Compounds)

Total Kjeldahl Nitrogen (TKN) content and the derivatives are important parameters used in evaluating the efficiency of sand and zeolite filters. **Table 3** and **Figure 4** illustrate the efficiency of the removal of Ammonia (NH3), Nitrates (NO3), and Nitrites (NO2).

Results obtained on the analysis of the filtered samples show high reduction in average concentrations of NH3, NO3, and NO2. The zeolite filter alone shows high efficiency in reducing the ammonia level from the average concentration of 174.47 $\pm$ 2.05 mg/L of raw wastewater to 0.52 $\pm$ 0.02 mg/L. On the other hand, the dual-media filter (sand + zeolite) has the highest efficiency in the reduction of Nitrates and Nitrites to average concentrations of 8.867 $\pm$ 0.231 mg/L and 8.667 $\pm$ 0.289 mg/L, respectively.

The system has shown outstanding efficiency in removing ammonia with the sand filter showing 99% efficiency, the zeolite 99.7%, and the hybrid system, 99.6%. These percentages are significantly higher compared to the current treatment facility in the hospital, whose efficiency in removing ammonia is at 88%. As far as Nitrates and Nitrites are concerned, the efficiency of the system (64% and 56%, respectively) is high since there is a repulsion between the negatively charged anions and the negative charge on the surface of the zeolite.

On the other hand, the current hospital WWTP has low efficiency in removing nitrites as indicated by the 27% increase in NO2 despite the 88% reduction in NO3. The superior efficiency of the zeolite filter in the system can be attributed to its ability to provide maximum surface for ion exchange. The high ion exchange is made possible by the chemical affinity of the clinoptilolite to ammonium ions due to an ionic diameter that corresponds with the zeolite structure. This is enhanced by the sand filter by regulating the flow distribution in order to avoid premature clogging, hence maximizing contact with the ammonia ions.

These results are in line with previous studies showing that the hydronium ion diameter is suitable for ion exchange within the zeolite channels due to their close match in diameters. TKN removal in this case may be due to nitrifying and denitrifying microorganisms present in the sand media. In addition, TKN removal efficiency increases as the flow rate reduces because of increased retention time. Van der Waals and hydrogen bonds ensure stability of pollutants in the zeolite micro-channels, preventing leaching of contaminants back to the effluent.

Table 3. Evaluate treatment performance according to pollutant category (Performance Matrix).

parameter	**Waste water**	**Sand filter**	**zeolite filter**	**Sand+zeolite filter**		
	Mean± St Dev.	Mean± St Dev.	Mean± St Dev.	Mean± St Dev.	F-Value	P-Value
NH3-N mg/l	174.4700a±2.05	2.0467b±0.00577	0.5200c±0.0200	0.6800 c±0.0200	21453.03	<0.0009**
NO2-N mg/l	22.000 a±1.000	18.667b ± 1.528	18.000 b±2.00	8.867 c±0.231	51.38	< 0.0009**
NO3-N mg/l	19.733 a±1.102	19.133 a±0.950	16.370 b±1.95	8.667c±0.289	51.75	< 0.0009**
SO4 mg/l	3133.0 a±80.800	2.50 b± 0.2000	1.67 b±0.1473	1.26 b±0.0100	45.03	<0.0009**
PO4 mg/l	25.370 a±2.05	2.900 b±0.400	2.800b±0.300	2.867 b±0.208	338.09	<0.00008**

Note: Different superscript letters ([a], [b], [c]) indicate statistically significant differences treatment stages according to Tukey's HSD post-hoc test ($p < 0.05$) . ** indicates $p < 0.00$.

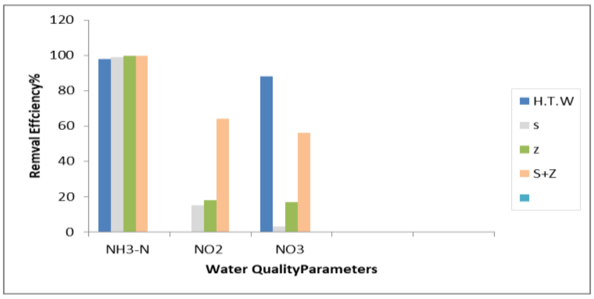

Figure 4. Removal efficiencies of nitrogenous species (NH_3, NO_3, NO_2) and TKN using single and dual-media filtration systems.

4.5. Phosphorus and Sulfate Removal Dynamics

The experimental results reveal a remarkable decrease in the concentration of total sulfate (SO4) and phosphorus (PO4-P) after their passage through the hybrid system (S+Z). The concentration of sulfates decreased from 3133.0 ± 80.8 mg/L of the raw sample to 1.26 ± 0.01 mg/L after filtration. Similarly, phosphorus, having an initial concentration of 25.37 ± 2.05 mg/L, had its concentration remarkably decreased in the zeolite media filter, with an average of 2.80 ± 0.30 mg/L, outperforming the separate sand media and hybrid systems.

Such efficiency in the removal process is mainly due to the presence of cation bridging. Natural zeolite has exchangeable cations including Ca2+ and Mg2+, which act as a bridge between the anions of phosphates and sulfates with the negatively charged surface of the zeolite. Additionally, phosphate can combine with calcium ions released from the zeolite structure to precipitate as calcium phosphate. This chemical precipitation of the particulate leads to the trapping of these particles inside the pores of the media including sand and zeolite. Both materials can be regarded as very precise mechanical filters capable of trapping sulfur and phosphorus ions bound to organic or colloidal particles.

The system exhibited a complete removal of sulfates and 88-89% of phosphates using separate sand and zeolite filter as well as the hybrid configuration. This was made possible due to the application of covalent bonds and chemical precipitation as shown in **Figure 5**. According to[34], the polyvalent cations present in the zeolite structure facilitate the attraction of negative anions through the formation of ionic bridges on the material's surface. Sand also played a vital role in trapping the sediment resulting from the salt reaction, thus enhancing the overall removal efficiency of the system.

On the other hand, the currently operating WWTP failed to show any efficiency in removing phosphorus as indicated by a 77% increase in the level of phosphorus in the final output. While the system managed to reduce sulfates by 96%, the lack of ability to remove phosphorus, which is among nutrients, will promote the growth of algae or bacteria resulting in eutrophication in the Al-Warrar Regulator. The presented results surpassed the performance of[35] who reported 78.94% maximum removal of TP at 120 L/h. This further confirms the efficient selective ion-exchange of zeolite as discussed by[36]. Utilization of sand as a support medium for zeolites lowers the cost of operation and is consistent with engineering knowledge on hybrid bioreactor efficiency.

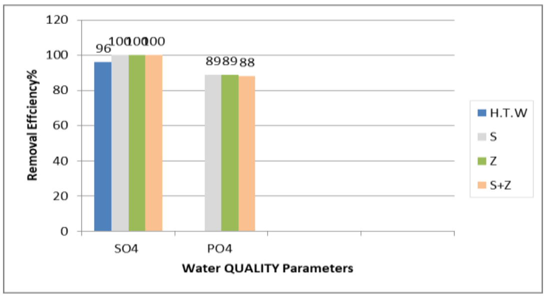

Figure 5. Removal efficiencies of Sulfates and Phosphates using sand and zeolite filtration systems compared to conventional treatment performance.

4.6. Heavy Metals and Chlorine Remediation

The analyses presented in Table 4 evaluate the effectiveness of integrated sand-zeolite filtering systems in lowering heavy metal concentration. There is statistically significant ($p<0.05$) decrease in iron (Fe), chromium (Cr), copper (Cu), zinc (Zn), and nickel (Ni) concentrations as well as in the content of residual chlorine after passing through the dual-media filter arrangement.

As can be seen in **Table 4**, the hybrid filtration system proved to be highly efficient for all studied parameters, providing full removal (100%) of iron and zinc, and making their concentration non-detected (zero). For the case of nickel ion, the highest reduction was observed when passing through the dual-media filter; the average nickel concentration in dual-media filtrate was 0.6133 ± 0.0115 mg/l, which was higher than single media filters of sand and zeolite. There was a pronounced decrease in the chromium concentration, varying from 0.000153 ± 0.000026 mg/l to 0.000195 ± 0.000005 mg/l compared to initial raw wastewater containing 0.00114 ± 0.00002 mg/l Cr.

Furthermore, there was a significant reduction of chlorine concentration, with its maximal efficiency in the dual-media filtration system. Chlorine concentration varied between 0.113 ± 0.006 mg/l and initial raw wastewater value of 3.403 ± 0.400 mg/l. Thus, one can conclude about the synergetic nature of this filter arrangement since the mechanical screening action of sand is supplemented with a high cation-exchange ability and adsorption capacity of natural zeolite.

Table 4. Evaluation of heavy metal and residual chlorine removal efficiencies across diverse filtration configurations.

parameter	West water	Sand filter	zeolite filter	Sand& zeolite filter		
	Mean± St Dev.	Mean± St Dev.	Mean± St Dev.	Mean± St Dev.	F-Value	P-Value
NI mg/l	1.2400 a±0.0400	1.1700 a±0.0300	0.8800 b±0.0346	0.6133 b±0.01155	258.86	< 0.00006**
Zn mg/l	1.5967 a±0.1650	0.3333 c±0.1528	0.4800 b±0.0200	0.0000 d±0.0000	112.92	< 0.00003**
Cu mg/l	0.00295 a±0.00010	0.000167 c±0.000058	0.000193 b±0.000003	0.000187 b±0.000006	11.46	< 0.003**

Fe mg/l	1.4000 a±0.2000	0.0800 c±0.0200	0.2300 b±0.0200	0.0000 c±0.0000	126.30	< 0.00004**
Cr mg/l	0.00114 b±0.00002	0.000195 a±0.000005	0.000185 a±0.000005	0.000153 a±0.000026	21.84	< 0.0007**
chlorine	3.403 a±0.400	0.690 b±0.320	0.657 b±0.006	0.113 c±0.006	100.30	< 0.00005**

Table 4. (*Continued*)

Different Superscripts ꜰ, ɹ, ʊ represent statistical differences between treatment phases according to Tukey's Honest Significant Difference Post-hoc test at $p < 0.05$. The text also mentions $p < 0.00$.

4.7. Comparative Analysis of Heavy Metal and Chlorine Removal Efficiencies

Based on the data from **Figures 5** and **6**, there were evident discrepancies amongst the different heavy metals analyzed. The hybrid media (S+Z) performed effectively in Nickel (Ni) removal; with an impressive efficiency level of 51%; equal to the maximum possible efficiency (58%) of the WWTP in the hospitals. However, the combination of the two media (S+Z) had an excellent efficiency of 100% for zinc removal while it was 86% in copper removal.

However, the current process in the hospital plant was inefficient in heavy metal removal. The maximum zinc efficiency was 77%, Chromium (Cr) was not successful, and levels of contamination increased by over 100%. Moreover, iron (Fe) removal efficiency was reduced to just 2%. In the hybrid method (S+Z), there was an excellent percentage of 87% and 100% for iron and chromium removal respectively. Residual Chlorine removal efficiency of the hospital wastewater treatment facility stood at 28%, compared to 80% and 81% of sand and zeolites individually. The efficiency of the hybrid method in residual chlorine removal rose up to 91%. In the zeolite and sand columns, the percentage is higher than the station's rates for chlorination, as illustrated in **Figure 7**. The results and observations showed that the best efficiency was recorded after 20 minutes. They also demonstrated a physical and chemical bond between the pollutants and the zeolite surface, according to the pathways described in the reference[33]. The van der Waals force of attraction and hydrogen bond ensure that contaminants do not easily get desorbed to the filtered water.

The research findings further support the ion exchange selectivity ability of zeolite, as mentioned in reference[36,37]. The addition of sand to facilitate filtration serves to optimize efficiency and reduce costs; an established engineering principle in bioreactors. According to reference[38], the sand filter technology proved to be effective in treating contaminated sulfurous water, where TDS, EC, phosphate, and Nitrogenous compounds had removal efficiency from 52% to 86%, enough to make it agriculturally safe. Finally, reference[39] supports the ability of fine sand to remove heavy metals (Cu, Zn, Fe, Cr) and nutrients from contaminated water. Coarse and mixed sands have a capability of reducing chlorine, calcium and potassium from wastewater.

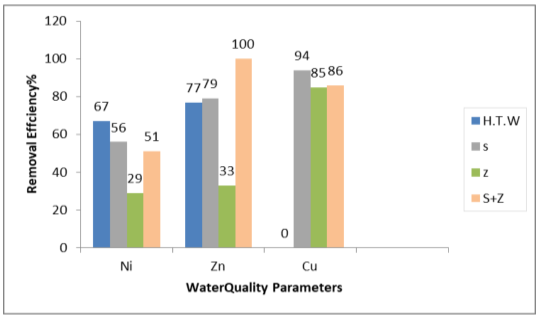

Figure 6. Comparative efficiency of different filtration media in the remediation of heavy metals (Nickel, Copper, and Zinc) from treated wastewater.

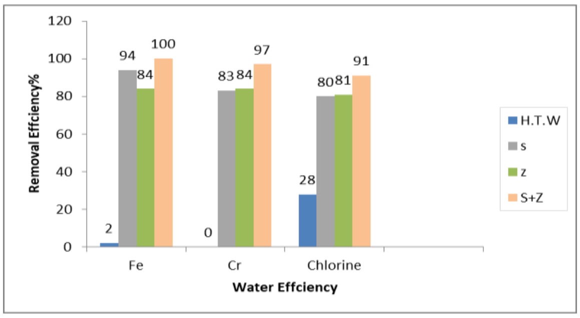

Figure 7. Comparative assessment of diverse filtration media for the removal of Iron, Chromium, and Residual Chlorine from treated wastewater.

4.8. Mechanisms of Heavy Metal Adsorption and Technical Constraints

The absorption process responsible for the separation of heavy metals from wastewater via natural zeolites depends primarily on ion-exchange operations. The heavy metal cations present in wastewater tend to get attracted to the negative charges present on the zeolite's outer surfaces, thereby displacing the exchangeable ions that exist in zeolites. Ion exchange operation, thus, plays a major role in isolating the heavy metals. Moreover, owing to the microporous nature of the natural zeolite, it becomes possible to absorb the metal ions not only on the outer surface but also in the micropores of zeolites. Thus, the absorption operation of metal ions takes place at more sites, thus increasing the adsorption capacity. Hence, it can be concluded that natural zeolites provide an efficient solution for dealing with wastewater containing heavy metals.

Despite its significant importance, the process of adsorption is accompanied by various limitations, which must be considered in the treatment process. The absorption efficiency depends mainly on the physicochemical characteristics of natural zeolites. For example, certain zeolite frameworks lack selectivity with respect to some heavy metal ions[40]. Moreover, competition for active sites among different ions may hinder the absorption process considerably.

5. Conclusion

This research paper brings to light the great prospects of using dual-media filters that combine sand and natural zeolites for cleaning hospital wastewater. The specific area of research covered by this paper is the wastewater discharged from the Ramadi Teaching Hospital for Maternity and Children. The main results of this research are listed below:

• Pollutant Profiling: The raw wastewater had increased amounts of different pollutants whose quantities far exceeded the maximum allowable discharge levels, thereby underlining the insufficiency of the existing sewage treatment processes.

• System Efficacy: The dual system involving sand and zeolite proved to be more effective in lowering water quality parameters such as TDS and EC than the current hospital water treatment plant. The unique physical and chemical characteristics of these materials provide an excellent adsorbent system that can be optimized by modifying the material itself.

• Targeted Removal: The natural zeolite proved to be extremely effective in eliminating the pollutants from the hospital effluent water, providing 93% BOD removal, 100% sulfates removal, and 84-85% heavy metal removal.

• Microbiological Remediation: The adsorption processes were very crucial in achieving immobilization and activation of microorganisms, which ultimately led to a decline in the total bacteria count (TBC) by 88%.

• Environmental Impact: This suggested solution effectively controls the primary cause of eutrophication (algal growth), namely, nutrients such as phosphorus and nitrogen. Through restricting the nutrients from entering the water bodies, the solution maintains the oxygen levels in the water that support aquatic organisms while turning the toxic discharge into a useful asset.

6. Practical Applications

1. Though this experiment has been carried out on a pilot plant scale in laboratory conditions, the impressive efficiencies obtained give a clear indication of how to proceed in many practical environmental engineering situations.
2. Decentralized Hospital Wastewater Units: A hybrid sand-zeolite technology could potentially be used on site as a polishing step in wastewater treatment for smaller or medium-sized health-care institutions within Ramadi. Because of its minimal energy requirements and utilization of local resources, it represents a plausible replacement for the aging municipal infrastructure, allowing for the effluent to meet discharge criteria before reaching the governing body of Al-Warrar.
3. Water Reclamation for Restricted Irrigation: The effluent from the wastewater treatment plant can be considered as reclaimed water since the removal efficiency of BOD and ammonia is 93% and 99%, respectively. This conclusion directly solves the problem of water scarcity in the region due to the depletion of the water levels of the Euphrates River.
4. Sustainable Aquaculture Systems: Its impressive ability to absorb harmful ammonia (99.7%) renders the zeolite especially useful in recirculating aquaculture systems (RAS), making it possible to increase the efficiency of water recycling and consequently minimize the environmental impact of fish farming.
5. Industrial Heavy Metal Pre-treatment: The achievement of 100% efficiency in the removal of iron and zinc demonstrates that such a setup can serve as an effective permeable reactive barrier in industrial areas, thereby ensuring the prevention of harmful metals from entering groundwater systems.
6. Integration into Green Building Infrastructure: The small size of the system allows it to be incorporated into green urban buildings for treating grey water from washing and bathing. This leads to the development of the idea of the circular water economy in urban areas.

Conflict of interest

The authors declare no conflict of interest.

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