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Sustainable Fabrication of Ca/Al-Layered Double Hydroxide (LDH)-Coated Sand from Marine Waste for Efficient Removal of Tetracycline Contamination in Water

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Abstract. The aim of this study was to formulate a reactive composite for treating the antibiotic contaminated water. Calcium-Aluminum (Ca/Al) bilayer hydroxide (LDH) nanoparticles were immobilized on the surface of inert sand to obtain an effective adsorbent for the removal of tetracycline (TC) from water. A sustainable approach was used to prepare these particles. From low cost alum, Al^{3+} ions were extracted and from shellfish waste, marine waste was used to extract calcium ions (Ca^{2+}) at an optimum concentration of 9000 mg/L of acetic acid. A surfactant SDS was used to improve the dispersion and uniformity of the coating of the nanoparticles on the sand surface. The synthesis conditions were systematically optimized by the study of the effects of the pH, the surfactant dosage, the calcium to aluminum (Ca/Al) molar ratio, and the quantity of sand added. It was found that the best parameter for the preparation of the adsorbent was pH 8, 0.1 g of SDS, 1:1 Ca/Al molar ratio and the ratio of sand to 50 mL solution, which is 1 g per 50 mL. In this scenario, the coated sand removed 54.1% of tetracycline after 3 h of contact in the presence of an initial concentration of 40 mg/L. The results showed that the surfactant SDS was much more effective than the surfactant CTAB for all the experiments. The successful deposition of Ca/Al-LDH nanoparticles onto the sand surface was confirmed through material characterization assays (XRD, FTIR and SEM) that revealed a lamellar structure, which greatly increased the surface reactivity of the inert substrate. The study introduces a sustainable marine biological waste-to-nanomaterials conversion process that offers a cost-effective, eco-friendly solution to address antibiotic pollution in wastewater.

1 Introduction

Antibiotic pollution of aquatic habitats is rapidly becoming an important issue in environmental protection. Antibiotics known as tetracyclines (TCs) were initially discovered in the 1940s and have been used therapeutically to aid in human health maintenance since

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the 1950s [1]. The antibacterial activity of TC is effective against the majority of bacteria, including both gram-negative and gram-positive bacteria. Although many developing nations have discouraged its use in human medicine due to the rise of resistant bacterial strains, TC is extensively used as a growth promoter in aquaculture, veterinary medicine, and livestock maintenance. It is also popular in developing nations due to its low cost.When animals are administered TC, there is an excretion of the antibiotic in its active form through feces at a rate of 70-90% and urine at a rate of 25-55%.Antibiotic byproducts seep into groundwater and surface runoff. Some aquatic creatures have their growth stunted, antibiotic-resistant microbial strains are created, and human endocrine systems are disrupted as a result of direct interactions with the steroidogenic pathway. Manure from cattle and poultry farms in Sri Lanka contains around 40% TC, 35% OTC, and 20% AMX, according to research.Since TC residues are detected in the effluents of certain chicken farms (ranging from 0.001 to 0.005 mg/L), it is imperative that these residues be removed before the effluents are released into the environment. Specifically, OTC residues are found between 0.001 and 0.004, while AMX residues are between 0.001 and 0.005 mg/L [2]. It is clear that adsorption is a simpler, cheaper, and less polluting method of removing TC from water when compared to other water treatment technologies like membrane processes, photochemical processes, electrochemical processes, photocatalytic and photo electrocatalytic processes, ozonation, and advanced oxidation technologies. For the adsorptive removal of antibiotics across all categories, many adsorbents have been employed; however, TC has proven to be illusive thus far. Research on adsorption typically makes use of affordable, naturally occurring, and abundant adsorbents like oyster shells. Oyster shells, which make up over a third of the world's bivalves production, are one easily accessible byproduct. Although these waste products have many potential uses, such as in fertilizers and arts and crafts, recycling or reusing oyster shells is not without its downsides. Pretreatment processes should be put in place to get rid of organic pollutants. Also, calcination is necessary for working with raw oyster shells, which is an extremely energy-intensive procedure. Consequently, it is highly desirable to find a way to transform such wastes into a product that has substantial economic worth. He emphasized that conventional nanoparticles—such as iron, copper, zinc, platinum, etc.—have far-reaching environmental impacts due to the reactive oxygen and nitrogen species they produce, which can influence cell physiology at concentrations higher than the threshold limit. Scientists have recently stepped into a new realm of nanotechnology, creating reactive materials that are more efficient, long-lasting, and inexpensive. These materials have the ability to impact the human immune system by depositing nanoparticles in organs like the brain and heart. One example of an environmentally friendly nanomaterial is calcium hydroxide, or $Ca(OH)_2$. It has many uses in catalysts, adsorbents, and sculpture treatment, among others. Researchers have also discovered that nano calcium hydroxide could be useful in water treatment, dentistry, and heritage conservation. The most common methods for producing nano-sized calcium hydroxide are solvent-and-ethanol processes, which involve high temperatures and pressure. Nanoparticles of calcium hydroxide, which are a byproduct, are quite unusual. Setting aside those issues, the lengthy purification procedure can occasionally end up costing a pretty penny. Find practical and affordable ways to recycle and reuse trash; that is the end goal. Making reactive materials that are more efficient, longer lasting, and cheaper is the new frontier of scientific investigation. Many studies were conducted to synthesize layered double hydroxides (LDHs) due to their potential uses in areas including electrochemistry, magnetization [3], and environmental protection. Laboratory and industrial-scale synthesis of LDHs is feasible due to their simplicity and low cost. Anions, cations, radionuclides, and dyes can all be extracted from water using these molecules. The chemical formula for LDH, which is an ion that preserves the interlayer charge, is [M2 1-xM3+ x (OH)2]x+(An-)x/n·mH2O. Here, M3+ and M2+ are trivalent and divalent metal ions, respectively, and x is the ratio of M3+ to the total of M3++M2+. Trivalent metals create

positively charged LDHs with a high point zero charge, although interlayer anions can exchange charges to maintain charge balance in the compounds. Numerous investigations have demonstrated that LDHs are capable of exchanging ions with interlayer anions and a wide range of chemical contaminants. This research aims to develop and analyze a novel composite material for use in wastewater treatment plants, namely one that coats filter sand with calcium/aluminium hydroxide (Ca/Al-LDH) nanoparticles. The unique production process of these nano-particles makes use of two sustainable and abundant resources: calcium, which is derived from oyster shells (a waste product of farming and marine operations), and aluminum, which is made from the common and affordable chemical alum. Specifically, tetracycline, an antibiotic, is to be extracted from wastewater-like water-based solutions. The idea of this research is to confirm that the composite material, Ca/Al-LDH Sand, is very efficient and selective in this particular method.

2. Aim of research

The first aim of this work is to convert non-reactive sand into a reactive material using the technique of anchored nanoparticles (LDH). The reaction between recovered calcium ions in oyster shells and recovered aluminum ions from the least expensive coagulant (alum) was aided by the use of sodium lauryl sulfate (SDS). Thus, sand coated with a double hydroxyn of calcium and aluminium. Sodium lauryl sulfate (SDS) was used to promote the reaction among calcium ions extracted from oyster shells and the aluminum ions that were obtained from the most economical coagulant, alum.

2.3 Materials and methods

2.3.1 Materials

The coating technique utilized the immobilized matrix of sand from filter units in the water treatment plant. The sand was purchased from a market, but it needs more washing and filtering to get it to a size between 0.6 and 1 mm. Sand had a specific gravity of 1.363 and a porosity of 0.45. As (Ca/Al)-LDH nanoparticles precipitate onto this sand's surface, they form new binding sites and functional groups; thus, this sand can be categorized as a low-reactive $Al_2(SO_4)_3.14H_2O$ material **(Faisal, Shihab, et al., 2021).** This will guarantee that composite sorbents with sufficient hydraulic conductivity for continuous mode operation and increased reactivity are manufactured. We bought the shells from a vendor in Basra governorate who sells used oysters. Calcium carbonate, namely the calcite phase, and trace amounts of other oxides such as potassium, silicon dioxide, magnesium oxide, and aluminum oxide make up the bulk of an oyster's chemical makeup. To prepare anything other than aluminum, the "shape" of $Al_2(SO4)_3.14H_2O$ is no longer obvious. The novel purification method involves the proportional addition of this exciter, which is an acceptor in water, to water. Use of SDS verified the encapsulation. Treatment**(Khan & Zareen, 2006)**. To conduct targeted analysis, a tetracycline (TC) mimic was utilized. Samarra Pharmaceutical Organization of Iraq supplied it. One liter of purified water and one gram of this pollutant were mixed at room temperature to produce a water mixture with 1000 mg/L tetracycline (TC) **(Henrique et al., 2022)**.

2.3.2 Calcium Extraction

Two main extraction solvents were used in comparative research to see how well they extracted calcium ions (Ca^{2+}) from oyster shell powder:1. This was done by using a Water

Based Chelating Agent: Ethylenediaminetetraacetate (EDTA). After dissolving 1.861 g and 5.58 g of EDTA in 100 mL of distilled water, respectively, 5 g oyster shell powder was added to the solutions to get the various concentrations. The second is an organic solvent and it is an acidic solvent: Acetic acid. Shell powder (5 g) and different volumes of acid (0.298 mL, 1.492 mL and 2.985 mL) [8] were added to a 100 mL distilled water solution. After that, we took care to stir the samples for as long as possible to remove all the reaction and calcium ions. After the extraction time, the solutions were filtered to remove any solid residue, which might have remained from the liquid extract. Table 1.1 gives the relationship between the quantity of solvent added and the final concentration of the calcium ions extracted. Using 2.985 mL of acetic acid produced the maximum concentration of Ca^{2+} ions, according to the data (9000 mg/L). This is an optimum number of calcium extraction which can be used in the process of coated sand production. Two main extraction solvents were used in comparative research to see how well they extracted calcium ions (Ca^{2+}) from oyster shell powder:

For this purpose a water-based Chelating Agent Ethylenediaminetetraacetate (EDTA) was used. The EDTA was dissolved in 100 mL of distilled water to form the 2 concentrations; 1.861 g and 5.58g. 5 g of oyster shell powder was then added to these concentrations to form the solutions.

The second component is an organic solvent and it is an acidic solution: acetic acid. 5 g of shell powder and different amounts of acid (0.298 mL, 1.492 mL, 2.985 mL) were added to 100 mL distilled water. Then we took care to mix the samples for as long as necessary to ensure that all of the reaction and calcium ions were removed. After the extraction time the solutions were filtered off the solid residue which was left from the liquid extract. Table 1.1 shows the relationship between the amount of solvent added to the mixture and the concentration of calcium ions obtained in the extract. The data shown is the highest concentration of Ca^{2+} ions when 2.985 mL of acetic acid was used. This is the correct quantity of calcium to use for extraction, and can be applied to the production of coated sand.

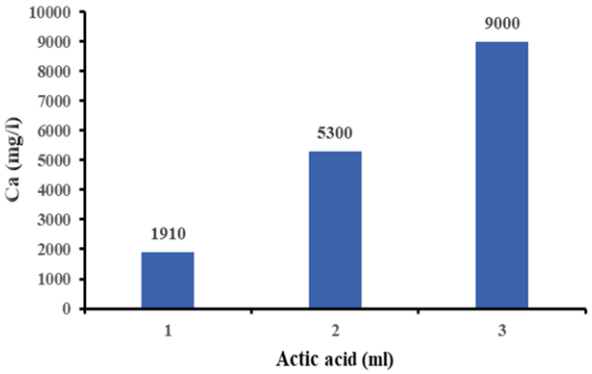


Fig.1. Calcium extraction setup from oyster shells using acetic acid and EDTA

The numbers in the first table are the calcium ion concentrations of various solutions. They demonstrate the variation of calcium content in relation to the type of solution (EDTA or acetic acid), the molarity of the solution and the volume of solution used. The data show the efficiency of each reagent in extracting calcium and that the higher the Ca concentration the more efficient the extraction.

Table 1. Calcium ion concentration results

S	Solution Type	Molarity (Mol/l)	Volume (ml or g)	Ca (mg/l)
1	EDTA	0.05	1.86 g	2100
2	EDTA	0.15	5.58 g	5100
3	Acetic	0.05	0.298 ml	1910
4	Acetic	0.25	1.492 ml	5300
5	Acetic	0.50	2.985 ml	9000

2.3.3Preparation of the Adsorbent (Coated Sand)

1. In 100 ml of distilled water, combine 5 grams of burned oyster shells with hydrochloric acid (in particular amounts). Set aside the mixture to sit at 24°C for 20 hours. Separate the calcium ion concentration from the mixture by filtering it.
2. To get a solution of aluminum with a given concentration, dissolve alum in distilled water. Combine the two solutions, keeping the molar ratio of calcium to aluminum constant at 1:5.
3. Finally, toss in some sand (about 0.5 to 2.5 grams) with the other ingredients. To the mixture, add surfactants (CTAB and SDS) **(H. Ahmed & Faisal, 2023)**in amounts ranging from 0 to 0.3 grams.
4. Sodium hydroxide should be added to the mixture in order to raise its pH to an alkaline range of 8 to 12. To create a layer of low-density hydrochloride (LDH) on top of the sand particles, mix the ingredients for three hours at 250 rpm.
5. Use distilled water to wash the covered sand and remove any contaminants. After separating and filtering the sand, dry it at 105°C for three hours.
6. One gram of the adsorbent was added to fifty milliliters of a tetracycline solution (40 mg/L) to assess its effectiveness**.**(Faisal, Ahmed, et al., 2021)

We examined the impacts of the following elements on the amoxicillin removal efficiency, which was the only statistic utilized to evaluate the coating process:

• Ratio of calcium to aluminum. • pH level when production is underway.
• How much detergent was used.

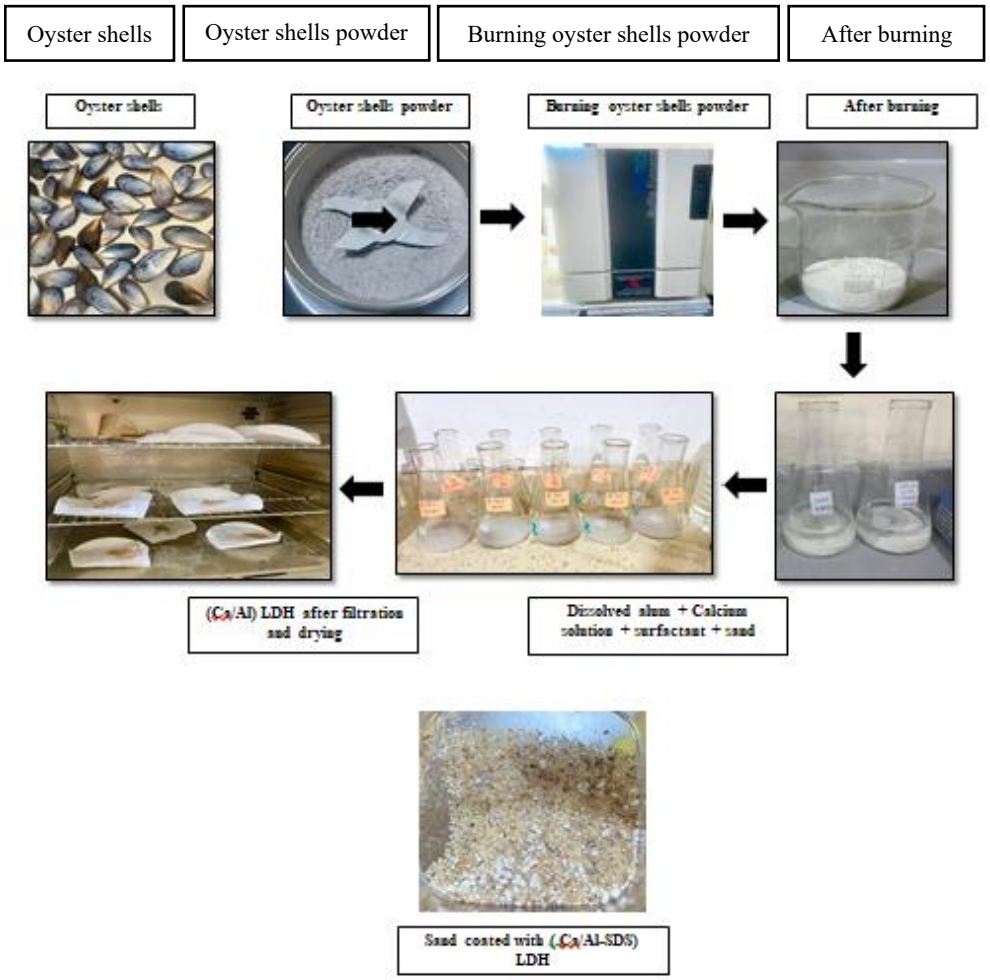


Fig.2. Graphical abstract of the synthesis of Ca/Al LDH nanocomposite

2.4 Operating standards for the material manufacturing testing program

2.4.1 Effect of Synthesis pH on Performance

A calcium/aluminum solution and surfactants (CTAB or SDS) were used to treat sand in order to create the coated adsorbents. A shift from 8 to 12 was made to the synthesis's pH. The effectiveness of the tetracycline removal process was tested by setting the initial concentration of tetracycline at 50 mg/L and a contact time of 3 h. The results revealed a non-linear correlation between the synthesis pH and the removal efficiency, with the highest removal efficiency (47.1% overall) from the highest pH (8) that was obtained for the SDS-modified sand (see Figure 3a). The performance decreased in the pH range 9-10, increased slightly at pH 11, and decreased drastically at pH 12. That is reflected in the fact that the pH of the reaction will have noteworthy influence on the production and properties of nanocoatings. Materials prepared with SDS were more effective than materials prepared with

CTAB for all values of pH considered. This indicates that SDS is the better choice for the job [11].

2.4.2 Effect of Surfactant Dosage

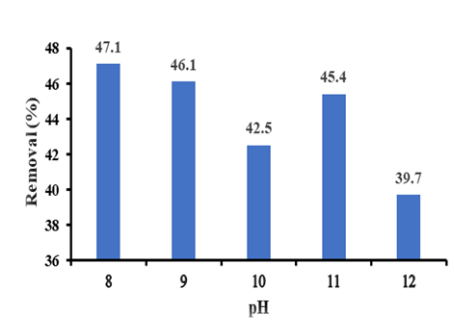
The influence of the coated sand preparation on the efficiency at a constant pH, 8.0, was investigated by varying the amount of CTAB and SDS surfactants. Normal doses were between 0.5 and 0 grams. From the figure 3b it is evident that the percentage of tetracycline removed is significant with the increase in the concentration of surfactant. The removal rate was achieved was 54.1% by using 0.1 grams of SDS. No effect was seen with smaller and larger doses. The clearance rates ranged from 48% to 52% and did not seem to be dose-dependent in terms of increasing CTAB efficacy. The non-linear relationship between the concentration of nanoparticles and the surface distribution and arrangement of the nanoparticles on the sand is likely to be more complex than the above mentioned.

2.4.3 Effect of Molar Ratio Ca/Al

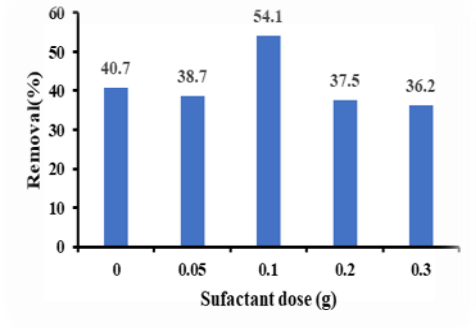
To determine the effect on the removal of tetracycline, researchers tested various calcium:aluminium ratios when creating coated sand. We looked at a few ratios between 1 and 5. Consistent nanoparticle layers on the sand surface are produced by a perfect 1:1 ratio, which achieves a maximum removal rate of 52.51%. The number of opportunities to trap tetracycline molecules and the surface area are both enhanced by the regular layers. If the ratio is altered, they are less able to absorb tetracycline when the ratio is altered because these layers become more irregular and disordered. This is why a ratio of 1:1 is the best one to use.

2.4.4 Effect of Sand Dosage on Adsorption Performance

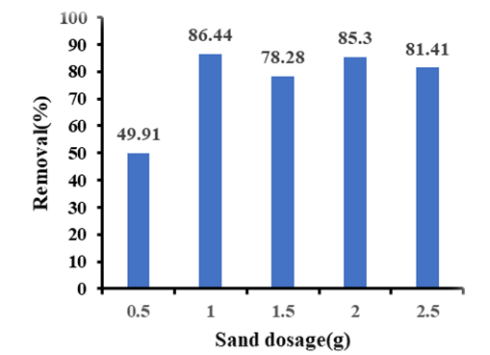
The effectiveness of the coating process for removing tetracycline was tested by varying the amount of sand used. The doses used in experiments were varied from 0.5 to 2.5 g/50 mL and all the conditions were favorable. Results demonstrating non-linear elimination are displayed in Figure 3d: Based on the observed performance change, it seems that the amount of effective nanoparticles is highly dependent upon the surface area of the sand. 1 g. is optimum. Higher doses lead to irregular aggregation of nanoparticles, and to low active adsorption sites at lower doses[11].



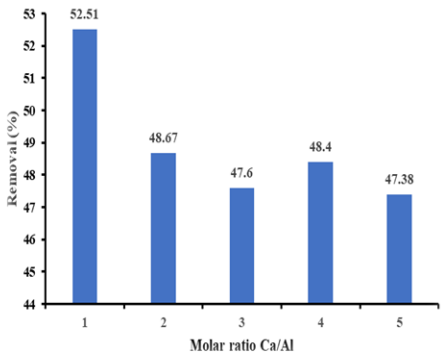
a. For synthesis (sand dosage = 4.5g/50ml, surfactant mass = 0.1g, Ca/Al=1)



b. For synthesis (sand dosage = 4.5g/50ml, Ph= 8, Ca/Al=1)



c. For synthesis (Sand dosage = 4.5g/50ml, pH= 8, surfactant mass =0.1g)



d. For synthesis (pH= 8, surfactant mass =0.1g, Ca/Al=1)

Fig. 3. The impact of a) pH, c) The (Ca/Al) Ratio, b) The Surfactant Dosage, d) Effect of Tetracycline Dosage on Sand Removal by Sand Coated with (Ca/Al-surfactant)-LDH under sorption conditions (length=3 hours, concentration=40 mg/L, sorbent) The dosage is 1 g/50 mL, and the conditions are pH 8, speed 250 rpm.

XRD Analysis

Before and after modification and adsorption the crystals phases of the materials were identified by X-ray diffraction (XRD) analysis. The diffraction pattern of the natural sand presented sharp and well-defined peaks at 2θ of 26.61°C and corresponding intensity of 3935 cts. The mineral quartz (SiO_2) is correlated with this peak from the JCPDS card, which indicates that the sand used is high crystalline. Significant increase of peak intensity was observed after treatment with the SDS, with peak intensity of 8789.93 cts at an angle of 26.64°. This has been attributed to the successful surface activation of the sand by the removal of impurities and the increase in active sites on the surface. But when the contaminant TC was added, a clear drop in intensity to 7007.92 cts was observed at the angle of 26.60° with very little change in angle. The decrease in the intensity with a constant angle proved that the TC particles were successfully adsorbed at the sand surface, and a thin layer of adsorbed TC particles covered the lower sand, which did not emit the signal. The stability of the angle indicates that the basic crystalline structure of the sand was not affected, thus the removal was not chemical [10, 12] but physical (surface adsorption) as can be seen in Fig. The X-ray diffraction (XRD) pattern of the three different samples is shown in the figure and the information obtained from this pattern is crucial in understanding the change in the structure caused by coating of sand with (Ca/Al-SDS) LDH and the influence of the adsorption process. The former pattern is related to untreated sand, with the peaks, i.e., at 2the = 26.6 and 2the = 39.2 showing the natural mineral phases, i.e. quartz and feldspar which are commonly found in natural sand. The changes in the following samples are compared to these peaks.

In the second pattern the sand surface is coated with (Ca/Al-SDS) LDH and the XRD profile displays the mineral peaks for sand in addition to the new peaks at 2θ = 11.2 and 2θ = 23.5 which are related to (Ca/Al-SDS) LDH coating. These extra peaks are evidence of successful development of the structure of the layered double hydroxide on the surface of the sand indicating that the process of coating the sand has changed the surface properties of the sand. The change is necessary in applications where the surface properties are crucial to the application, such as in catalysis or adsorption.

The sand-coated (Ca/Al-SDS) LDH sample that has gone through an adsorption procedure. The XRD pattern indicates changes in the intensities of the peaks and possibly new peaks

which were not observed in the last two samples. A typical example is the peak at 2 theta = 12.80 of the third pattern that shows the changes of the LDH structure, as molecules or ions could have intercalated between the layers or structural changes could have occurred, leading to changes in crystallinity. Such changes in the XRD patterns are indicative of modification to the material in contact with adsorbates that is relevant for the knowledge of the material's interaction with various materials in environments and industrial applications. Overall, the three XRD patterns show the structure of the untreated sand and of the two kinds of sand coated with (Ca/Al-SDS) LDH and the resulting changes which are attributed to adsorption. The results highlight the importance of (Ca/Al-SDS) LDH in improving the surface characteristics of sand, and its application in many other areas, such as environmental remediation and catalysis.

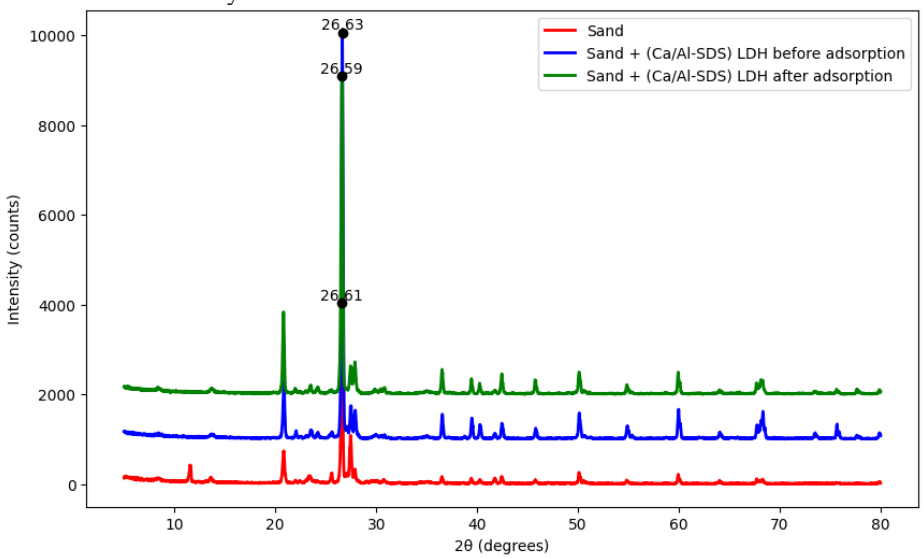


Fig.4 The XRD patterns of sand and sand coated with (Ca/Al-SDS) LDH.

3. FTIR Analysis

To determine the functional groups involved in the adsorption process on the sand surface, FTIR spectroscopy was conducted. The spectrometer for natural sand exhibited a broad band at 3445cm-1, which is attributed to the vibration of hydroxyl (OH) group of water molecules that may be adsorbing onto the surface, a sharp band at 1068cm-1 and a band at 778cm-1 which are attributed to the Si-O-Si bond confirming the presence of quartz. For the SDS coated surfaces a broadening and increase in intensity of the peak at 3430 cm-1 was seen due to an increase in surface hydroxyl groups and the presence of water molecules between the layers. In addition, new peaks were found in the region of 400-800 cm^{-1}, which were identified as vibrations of the oxygen – metal bond (M – O) and the oxygen – hydrogen bond (M – OH), with M = Ca or Al, indicating the deposition of the nanoparticles on the surface of the sand. After the adsorption, a distinct modification in the spectroscopy occurred, showing the presence of new peaks at 1050-1150 cm^{-1}, which were related to the vibrations of the S=O, C-N or C-H bonds in the structure of the TC contaminant. In addition, a change in some of the peaks of the oxygen-metal bonds in the 400–800 cm^{-1} region was noted, which corresponds to the interaction of such bonds with TC molecules and their surface anchorage via surface complexity, ion exchange and hydrogen bonding [10, 11, 13], as depicted in Fig.

The FTIR spectra shown in Figure 7 give information about the chemical structure and surface functional groups of three samples: pristine sand (Sample 1), sand modified with Ca/Al-layered double hydroxide (LDH) before adsorption (Sample 2), and sand + Ca/Al-(LDH) after adsorption (Sample 3). Sample 1, which is a pristine sand, shows absorption bands at 3432.67 cm^{-1} due to O–H stretching vibrations of surface hydroxyl groups, at 1079.94 cm^{-1} assigned to Si–O stretching, at 777.17 cm^{-1} assigned to Si–O bending, and at 418.48 cm^{-1} assigned to lattice vibrations of quartz.

The spectrum of sample 2 (sand+Ca/Al-(LDH) before adsorption) shows changes in the spectrum with the O–H stretching peak being shifted slightly to 3405.67 cm^{-1}, which is due to hydrogen bonding with interlayer water molecules. The successful incorporation of the Ca/Al-LDH onto the sand surface is demonstrated by the appearance of a new band at 1620.88 cm−1, assigned to hydroxyl bending in the LDH structure, and the Si–O/M–O overlapping vibrations at 1080.91 cm−1 and 778.13 cm−1, respectively. Other bands at 693.28 cm^{-1} and 468.01 cm^{-1} are related to the vibrations of metal–oxygen in the LDH structure.

Sample 3 (sand + Ca/Al-(LDH) after adsorption) shows other changes in spectra after adsorption. A lower intensity O–H stretching peak is observed at 3429.78 cm-^{1}, indicating that the surface hydroxyl groups are consumed in the adsorption process. The Si–O stretching mode is observed at 1005.7 cm^{-1}, the bending modes appear at 777.17 cm^{-1}, and new bands are observed at 420.41 cm^{-1} and 363.24 cm^{-1}, which are due to interactions between the LDH structure and the adsorbed species. These changes and intensity changes affirm that the surface chemistry of the composite has been altered due to adsorption and that the composite is effective at interacting with the target molecules. FTIR spectra provide a detailed molecular level characterization of material, and in general, confirm the structural integrity of sand, successful modification with Ca/Al-LDH and the presence of active sites involved to the adsorption process.

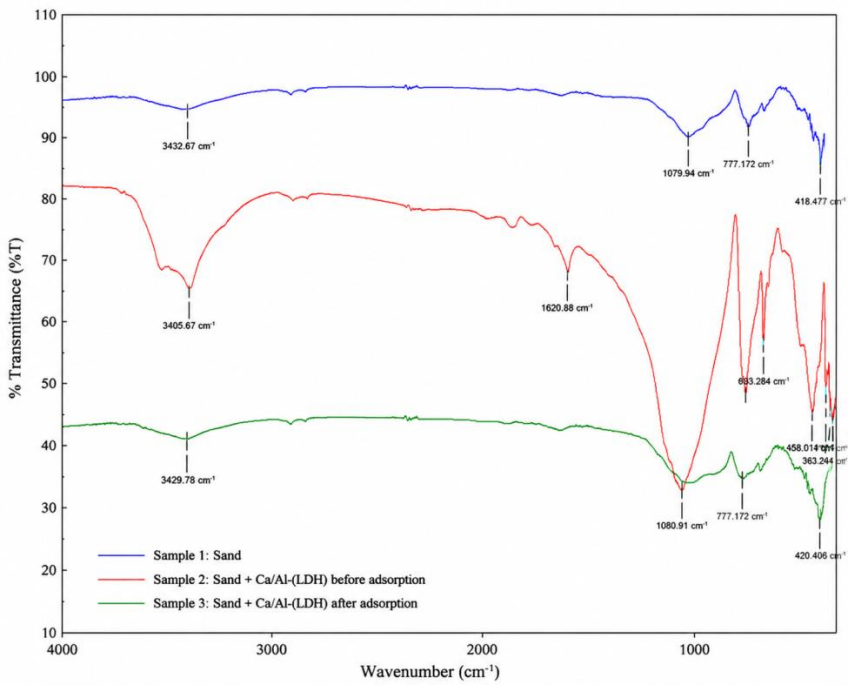


Fig. 5 FT-IR Analysis for Virgin Sand as well as Coated Sand with (Ca/Al-SDS) before and after Interaction with Tetracycline

SEM analysis: Scanning electron microscopy (SEM) images of the treated natural surface and natural quartz grains showed a rough, unstable surface, exhibiting micro-cracks and gaps, and a surface that was naturally treated with vitreous deposition. After SDS creation, the surface of the treated natural sample was completely covered with a distinct layer (a plate-like layer) formed by aggregated nanosheets of non-open orientations and sizes, which increased the surface area and confirmed the successful deposition of LDH particles.After SDS creation, the surface of the treated natural sample was completely covered with a distinct layer (a plate-like layer) formed by aggregated nanosheets of non-open orientations and sizes, increasing the surface area and confirming the successful deposition of LDH particles. In the post TC-adsorption state, the inter-lamellar spaces were filled completely and extra layers as well as small aggregates were observed on the original lamellar structure, which demonstrates a successful adsorption process in which the TC particles are attached to the surface [10]. The SEM for the sand, sand coated with (Ca/Al-SDS) LDH is shown in the figure 6. The TEM images in Figure 7 show the sand coated with (Ca/Al-SDS) layered double hydroxide (LDH). The overall morphology and distribution of the LDH coating on the sand particles are revealed in the left image with a scale bar of 0.4 μm, indicating thin plate-like structures and some agglomerates. The image on the right at a higher magnification and with a scale bar of 200 nm, shows the finer details of the LDH layers, including their nanometer-scale thickness and uniform coverage on the sand surfaces. These images confirm the successful deposition of the Ca/Al-SDS LDH on the sand substrate and give an idea on the micro- and nanostructural features of the coating.

Fig. 6 SEM images for (a) virgin sand (b) coated sand (c) coated sand after interaction with Tetracycline antibiotic.

Fig. 7 The TEM image for the sand coated coated with (Ca/Al-SDS) LDH.

4. Comparative studies

Inert sand and humic acid nanoparticles could be easily combined to form a permeable reactive barrier (PRB), as stated by Ayad A.H. Faisal et al. (2020). The treatment of groundwater polluted with cadmium and copper ions is possible using this approach. Making

humic acid from sewage sludge—a waste product of wastewater treatment facilities—is one use of sustainable development practices. The batch test findings demonstrated that the humic acid coated sand (CSHA) had a removal effectiveness larger than 98% when subjected to the following conditions: starting concentration of 10 mg/L, sorbent dose of 7, initial contact length of 1 hour, initial pH of 0.25 g/50 mL, and agitation speed of 200 rpm. According to the sorption data that followed a pseudo-first-order model, physisorption was the main way that metals and CSHA interacted. The maximal sorption capacities for copper were 87.5 mg/mg/g and for cadmium they were 18.9 mg/g. Research into their properties has shown that humic acid nanoparticles are present on the beach. Comsol Multiphysics 3.5a provided a thorough explanation for the observed mobility of the metal ions that were used in the experiment. Measurements and estimations from the models showed that concentration and flow rate dropped off at a specific bed depth, which slowed the movement of the metal front. An initial concept for this project was to use cement kiln dust and alum, two inexpensive chemicals, to make layered double hydroxide (LDH) with calcium and aluminum, with the goal of reducing the industry's financial and ecological impact.The original idea behind this effort was to reduce the financial and environmental imprint of the cement business by making calcium and aluminum based layered double hydroxide (LDH) from cement kiln dust (CKD), a waste product of the industry, using alum, a cheap chemical. An innovative sorbent called "sand coated with (Ca/Al)-LDH" was created by immobilizing the compound's pH 7 gel solution onto sand surfaces and then determining its identity by X-ray diffraction (XRD) techniques. The designed sorbent required an 8-pH, a 2-to-1 Ca/Al molar ratio, and 1 g/100 mL sand dosage for optimal results when reacting with Congo red dye. The developed material effectively extracted the Congo red dye from water samples in both batch and continuous tests, as shown by the experimental results. Dye concentrations of 50 mg/L were used to start the batch test. Assuming a starting pH of 7, the reaction was allowed to run for 60 minutes at a speed of 200 rpm with a sorbent concentration of 0.2 g/50 mL. A maximum capacity for adsorption of 60.64 mg/sorption was determined based on kinetic measurements that were optimally generated using the Langmuir and pseudo second-order models, respectively. Chemisorption has removed the dye. According to characterization experiments, the freshly created nanoparticles on the beach also significantly affected dye sorption. Finally, the output sorbent's efficiency was significantly enhanced by increasing the packed column sorbent and decreasing the flow rate, whereas the input contaminant concentration had no effect. When the solute transport equation was solved using numerical models in the COMSOL program, the results were very consistent with the measured breakthrough curves.

By mixing ferric ions with wastepaper sludge ash, Osamah Al Hashimi et al. (2023) created a new and environmentally acceptable adsorbent material known as calcium ferric oxide silica sand (CFO-SS). This technique has successfully removed TC from polluted water. Several batch and fixed bed experiments were conducted after drying the synthetic sand at 95 °C to determine the optimal conditions. The results show that growing the concentration gradient between the solid and liquid phases improves the capability of the CFO-adsorption SS. After three hours of agitation at 200 rpm, the results demonstrated that the new adsorbent could remove more than 90% of the TC from 50 mL of simulated groundwater with a pollutant concentration of 50 mg/L. Adsorption isotherm results were in agreement with the Langmuir isotherm model, and loading capacity was observed to be 21.96 mg/g at pH 7. The absorption kinetics were best described by the pseudo-second-order model. Various adsorption mechanisms were suggested, including hydrogen bonding, electrostatic interaction, intraparticle diffusion, and cation-π interaction. More research revealed that the newly produced oxides on silica sand are vital in supplying the required support for TC adsorption. Sorbent formation in the packed column, together with lower TC intake flow rate and concentration, significantly enhances sorbent longevity, according to experiments with

fixed beds. We were able to compare the models by obtaining the square root number (R^2) of the measured breakthrough curves. The most significant values were generated by the Adams-Bohart and Clark models, which were the best fits. In conclusion, it is worth noting that, according to CFO-SS's efficacy in TC adsorption performance, the recently produced reactive material is unquestionably an effective and environmentally benign chemical for TC removal. Groundwater with high TC concentrations may benefit from this in the long term. This study introduces a new sorbent composed of sodium alginate beads and Ag/Fe nanoparticles that can be used in a continuous configuration of the permeable reactive barrier (PRB). Amoxicillin (AMX)-polluted simulated groundwater can be treated with the sorbent. The beads are made from solid waste, namely pomegranate peels and sesban tree leaves, in order to follow the ideals of sustainability. Nanoparticles made of silver and iron layered double hydroxides were immobilized with sodium alginate to form the sorbent. The utilization of iron ions precipitated from sesame tree peels and pomegranate tree peels, respectively, was employed to produce these particles. A molar ratio (Ag/Fe) of 0.5, a solution pH of 9, and a dosage of 7 g of silver to iron nanoparticles per 100 mL of sodium alginate were the ideal conditions for synthesizing the bead for excellent AMX removal efficacy. Testing on the beads for characterization revealed that the nanoparticles could sorb antibiotics. Based on the results, PRB can stop AMX from migrating, and its lifespan is inversely related to inlet concentration and water flow rate, directly proportional to bead thickness, and proportionate to the inlet concentration. According to the results of the ongoing AMX removal tests, the "Bohart-Adams," "Yan," "Belter-Cussler-Hu," and "Clark" models have been fitted. These models have been used to construct the "breakthrough curves" for the transport of pollutants along the packed beads. The Belter-Cussler-Hu model is more suited for representing the outcomes of continuous experiments.

A QS-Fe/Pb nanocomposite was created by Noor Alaa Abdul Husain and Ziad Tark Abd Alib (2023) by mixing quartz sand (QS) with (Fe/Pb) nanoparticles synthesized in-situ using pomegranate peel extract. Remediating groundwater contaminated with ciprofloxacin (CIP) and copper (Cu (II)) was achieved in both batch and continuous modes by using it as a reactive material in a permeable reactive barrier (PRB). Surface area analysis, XRD, FTIR, SEM, EDX, and TEM were used to determine the nanocomposite's characteristics. In order to achieve a 99% eradication percentage in both batch and continuous modes, researchers examined several factors while assessing the nanocomposite's reactive bed activity. Two isotherm models (Langmuir and Freudenberg) and three kinetic models (intraparticle diffusion, second order, and pseudo-first order) and five breakthrough curve models (Thomas-BDST, Bohart-Adams, Belter-Cussler-Hu Model, Yan, and Clark) were made use of in total. The findings showed that the Freundlich and pseudo-second-order models were more appropriate for the batch experimental data when it came to the adsorption capacities of Cu (II), with a value of 15.2 mg/g and 9.8 mg/g, respectively. On the other hand, the Clark model performed admirably with the continuous experimental data. The manufactured Nanocombettes display all the desired characteristics as a reactive PRB material, as indicated by the results.

Table 2. The comparative studies for different pollutants, adsorbents, and removal efficiency.

Author (year)	Adsorbent material	Pollutant	Optimum conditions	Maximum Removal capacity
Ayad A.H. Faisal et al. (2020)	coated sand by humic acid (CSHA)	copper and cadmium ions	contact time1h sorbent dosage= 0.25g/50mL initial concentration =10mg/l	98%
Ayad A.H. Faisal et al. (2021)	sand coated with (Ca/Al)-LDH	sorbent-Congo red dye	pH 8, (Ca/Al) molar ratio 2 and dosage of sand 1 g/100 mL initial concentration =50mg/l	90%
Osamah Al-Hashimi et al. (2023)	calcium ferric oxide silica sand (CFO-SS)	tetracycline antibiotic	pH 7 pollutant dose of 50 mg/L in 50 mL, speed of 200 rpm	90%
Noor Alaa Abdul Husain, Ziad Tark Abd Alib (2023)	QS-Fe/Pb nanocomposite	ciprofloxacin (CIP) and copper (Cu (II))	Co=50mg/l, Speed=200 CIP:Time =70, PH =7 Cu:Time=120, PH=6	999%
Dalal Ghanim Yahia and Ayad A.H. Faisal (2025)	Ag/Fe – nanoparticles – sodium alginate beads	Amoxicillin (AMX)	molar ratio (Ag/Fe) = 0.5, pH=9, dosage=7g per100mL	95%

5. Conclusions

An effective adsorbent was fabricated by fixing the aluminum hydroxide and aluminum-rich aluminum nanoparticles (Ca/Al-LDH) on a sand surface, in the presence of the surfactant SDS, using the calcium ions extracted from oyster shell and alum-coated ions. The pH 8 and 0.1 g SDS dosage and Ca/Al molar ratio of 1:1, and 1 g/50 mL sand were used to improve the removal efficiency of tetracycline. Successful deposition and surface plate formation on the surface of sand were confirmed by FTIR, XRD and SEM scans which increased the surface area and granularity of the sand. The promising and progressive work suggests the possibility of converting marine oyster shells into useful nanoparticles to use in water-based drug administration.

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