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Proceeding Paper

Enhanced Pollutant Adsorption and Antibacterial Activity of a Hydrogel Nanocomposite Incorporating Titanium Dioxide Nanoparticles †

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Abstract: This research delineates the synthesis and subsequent application of a hydrogel nanocomposite enriched with titanium dioxide (TiO_2) nanoparticles as an adsorbent for pollutants and an antibacterial agent. The nanocomposite was prepared using a hydrothermal method, facilitating the efficient incorporation of TiO_2 nanoparticles. Physicochemical characterizations revealed the nanocomposite's augmented adsorption capabilities, specifically for pollutants such as Congo red dye (CR), Amoxilline drug (AMX), and Chlorophenol (CPH). Notably, the study demonstrated that the nanocomposite could be completely regenerated and desorbed in water, attesting to its potential for recyclability. The antibacterial potential of the nanocomposite was also investigated, demonstrating significant efficacy against Gram-negative bacteria (*E. coli* and *Klebsiella* spp.) compared to Gram-positive strains. The findings of this study emphasize the potential applicability of the hydrogel nanocomposite as an efficient, reusable agent for pollutant removal and antibacterial activity, providing pertinent insights for environmental remediation and biomedical applications.

Keywords: hydrogel nanocomposite; titanium dioxide nanoparticles; pollutant adsorption; antibacterial activity; regeneration

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1. Introduction

Hydrogels are a type of polymer chain known for their exceptional hydrophilic properties. When crosslinked, these chains form hydrogels that exhibit an impressive capacity to swell in aqueous solutions. A distinct characteristic of hydrogels is their ability to encapsulate pollutants, effectively trapping them for prolonged periods without dissolution [1,2]. Clay materials are naturally occurring adsorbents that are classified based on the variations in their layered structure. Examples of clay types include smectites (e.g., montmorillonite, saponite), serpentine, kaolinite, mica (illite), pylophyllite (talc), vermiculite, and sepiolite [3]. Clays possess diverse physical properties such as hardness, plasticity, and cohesion. They are also composed of various compounds like alumina, calcium, silica, iron, and magnesium oxides [4–7]. Titanium dioxide (TiO_2) naturally occurs in three main crystalline phases: brookite, anatase, and rutile, with rutile being considered thermodynamically more stable than the others. Titanium dioxide is favored for its cost-effectiveness, safety in production, and electrochemical properties. Additionally, TiO_2 has been applied in areas like microbial and UV protection, and more notably as a powerful photo-catalyst for decomposing dyes and pharmaceuticals [8–10]. Recent research has shown the benefits of integrating titanium dioxide particles with hydrogels in the removal of various water pollutants, such as dyes, pharmaceuticals, heavy metals, and hazardous organic compounds. This incorporation enhances the recovery and pollutant removal efficiency of the hydrogels [11–14]. Staphylococcus aureus is a round-shaped, Gram-positive bacterium that is often found on the skin and upper respiratory tract. This facultative anaerobic organism can thrive without the need for oxygen, and although it normally coexists as part of the human microbiota, it can become an opportunistic pathogen. Staphylococcus aureus is frequently associated with a variety of infections, including skin abscesses, respiratory infections, and food poisoning. Certain strains of this bacterium can become particularly dangerous through the production of potent protein toxins and the expression of cell-surface proteins that bind to and inactivate antibodies [15,16].

2. Methods

2.1. Preparation of TiO_2 Nanoparticles by Hydrothermal Synthesis

Titanium dioxide nanoparticles were synthesized using hydrothermal treatment of titanium(IV) bis (ammonium lactate) dihydroxide. This procedure was performed in a 250 mL Teflon cup. For each experiment, 10 mL of titanium(IV) bis (ammonium lactate) dihydroxide aqueous solution and ammonium hydroxide (NH_4OH) were mixed together. Subsequently, distilled water was added to this mixture until the final volume of 100 mL was achieved. The resultant solution was thoroughly mixed for an additional five minutes, as depicted in Figure 1.

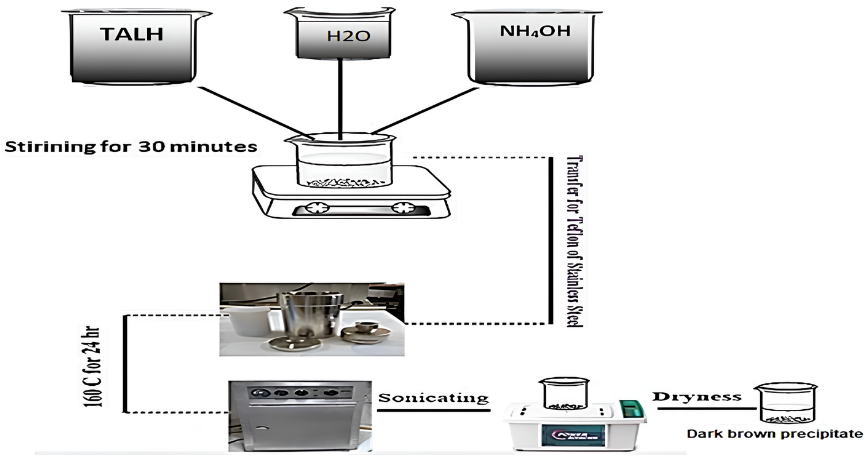

Figure 1. Preparation of TiO2 nanoparticles.

2.2. Preparation of Hydrogel

The hydrogel was prepared by initially dissolving 2 g of sodium alginate (NaA) in 120 mL of distilled water with continuous stirring for 1 h. Simultaneously, 4 g of clay was dissolved in 40 mL of distilled water under constant stirring for 30 min. The sodium alginate solution was then combined with the clay solution, and the mixture was stirred for an additional hour until homogenization was achieved. The resulting solution was then added drop by drop into a second solution containing calcium chloride ($CaCl_2$) and the prepared TiO_2 nanoparticles. This was stirred for another hour. After this process, the final product was washed several times with distilled water, dried, ground, and then utilized in subsequent experiments.

2.3. Bacterial Biological Activity Test

Gram-negative bacteria (*E. coli*, and *Klebsiella* spp.) and Gram-positive bacteria (*Staphylococcus aureus* and *Streptococcus epidermidis*) were obtained from the Department of Life Sciences, College of Science, University of Babylon. Hinton agar and Mannitol salt agar were used as cultivation, isolation, and differentiation media for these bacteria.

2.4. Preparation of Standard Solutions for Bacteria

Mueller–Hinton agar medium was prepared by dissolving 37 g of the culture medium in 1 L of distilled water. The mixture was heated until the agar dissolved completely. This culture medium was then autoclaved at a temperature of 120 °C for 15 min. The medium was poured into sterilized Petri dishes, using approximately 15–20 mL per plate, and allowed to solidify. To verify the sterility of the medium, the dishes were incubated for 24 h at 37 °C.

2.5. Bacterial Isolates

In this study, two Gram-positive bacteria (Staphylococcus aureus and Staphylococcus epidermidis) and two Gram-negative bacteria (*Klebsiella* spp. and *E. coli*) were used. The disc diffusion method was employed to test these four pathogenic bacterial isolates against four surfaces, namely: NaA-Clay, NaA-Clay-TiO_2, TiO_2, and clay. For each surface, 0.1 g and 0.2 g samples were taken, and 100 µL was added to a 6 mm diameter well in a culture Petri dish. The dishes were then incubated for 24 h at 37 °C, after which the zone of inhibition was measured.

3. Results and Discussion

3.1. Physicochemical Characterization of Adsorbents Surfaces

Figure 2a,b show the Field Emission Scanning Electron Microscope (FESEM) images of the NaA-Clay surface before and after loading with titanium oxide, respectively. Before loading, the surface has numerous active sites, while after loading with titanium oxide, the active sites are largely filled, making the surface more dense [1,17,18].

The Energy-Dispersive X-ray (EDX) spectrum of the hydrogel (Figure 2c) confirms the absence of titanium oxide nanoparticles (TiO_2NPs). After loading the TiO_2NPs, the EDX spectrum (Figure 2d) shows peaks corresponding to titanium and oxygen, confirming successful loading [19]. The X-ray Diffraction (XRD) spectrum reveals the structural properties of the hydrogel, indicating that the composite is amorphous with nanocrystalline features (Figure 2e) [17,20].

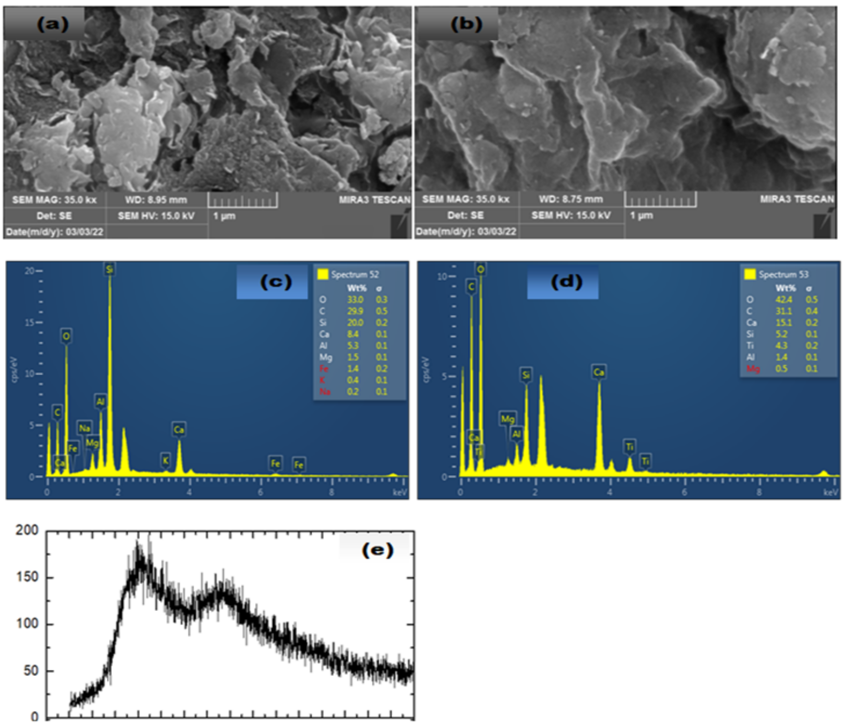

Figure 2. (**a**) FESEM images of NaA-Clay (**b**) FESEM images of NaA-Clay/TiO_2, (**c**) EDS of NaA-Clay, (**d**) EDS of NaA-Clay/TiO_2, (**e**) XRD of NaA-Clay/TiO_2.

3.2. Regeneration of Hydrogel Nanocomposite

Regeneration of the hydrogel after sorption is a crucial economic factor in the treatment process. It helps in understanding the mechanism of pollutant removal and regeneration, potentially reducing operational costs and preventing secondary pollution. Desorption studies for three pollutants (Congo red dye (CR), Amoxicillin (AMX), and Chlorophenol (CPH)) were carried out using different desorption agents at several concentrations (0.01, 0.05, 0.1 N) like NaOH, H_2SO_4, HCl, H_3PO_4, HNO_3, methanol, ethanol, and water [21,22]. Complete regeneration of the hydrogel nanocomposite was achieved using water, as shown in Tables 1–3.

Table 1. Comparison of desorption efficiency of several types of solutions for the CR dye onto the surface of hydrogel nanocomposite.

Regeneration and Desorption (0.01 N)	E%	Regeneration and Desorption (0.05 N)	E%
Fresh	92.09	Fresh	92.09
Water	92.09	Water	92.09
Ethanol	80.12	Ethanol	88.87
H_3PO_4	82.23	H_3PO_4	80.22
HCl	78.77	HCl	70.77
H_2SO_4	75.66	H_2SO_4	68.11
HNO_3	66.9	HNO_3	59.65
Methanol	60.11	Methanol	57.56
NaOH	52.11	NaOH	40.2

Table 2. Comparison of desorption efficiency of several types of solutions for the AMX drug onto the surface of hydrogel nanocomposite.

Regeneration and Desorption (0.01 N)	E%	Regeneration and Desorption (0.05 N)	E%
Fresh	84.87	Fresh	84.87
Water	84.87	Water	84.87
Ethanol	80.22	Ethanol	82.87
H_3PO_4	77.34	H_3PO_4	75.87
HCl	70.77	HCl	67.87
H_2SO_4	65.77	H_2SO_4	56.76
HNO_3	60.55	HNO_3	49.98
Methanol	55.11	Methanol	44.56
NaOH	50.11	NaOH	42.44

Table 3. Comparison of desorption efficiency of several types of solutions for the CPH onto the surface of hydrogel nanocomposite.

Regeneration and Desorption (0.01 N)	E%	Regeneration and Desorption (0.05 N)	E%
Fresh	80.29	Fresh	80.29
Water	80.29	Water	80.29
Ethanol	75.12	Ethanol	78.57
H_3PO_4	72.76	H_3PO_4	62.87
HCl	66.87	HCl	53.87
H_2SO_4	59.98	H_2SO_4	45.98
HNO_3	50.87	HNO_3	37.87
Methanol	47.11	Methanol	35.55
NaOH	44.65	NaOH	30.65

3.3. Biological Activity

This study evaluated the antibacterial activity of various surfaces against two types of bacteria: Gram-positive (*Staphylococcus aureus* and *Staphylococcus epidermidis*) and Gram-negative (*Klebsiella* spp. and *E. coli*). The antibacterial activity was tested using four different surfaces: NaA-Clay-TiO_2 NPs hydrogel composite, NaA-Clay hydrogel, TiO_2 NPs, and clay.

Figure 3 represents the antibacterial activity of the four surfaces against the bacterial strains. Remarkably, the NaA-Clay-TiO_2 NPs and NaA-Clay surfaces demonstrated significant antibacterial activity against the Gram-negative bacteria (*Klebsiella* spp. and *E. coli*), with an inhibition zone of 20 mm. These surfaces exhibited more robust antibacterial activity compared to TiO_2 NPs and clay, particularly against Staphylococcus aureus and Staphylococcus epidermidis [23]. The TiO_2 NPs and clay surfaces, on the other hand, exhibited limited antibacterial activity against both Gram-positive and Gram-negative bacteria. Figures 4 and 5 illustrate the inhibition zones for the four compounds at weights of 0.1 g and 0.2 g. The NaA-Clay/TiO_2 NPs composite displayed the most antibacterial activity, 20 mm against *E. coli* and 15 mm against *Klebsiella* spp. This compound was more effective against Gram-negative bacteria than Gram-positive bacteria [23–25]. NaA-Clay had antibacterial activity against E. coli (7 mm) and *Klebsiella* spp. (6 mm), but no activity against Staphylococcus aureus and Streptococcus epidermidis, indicating a more significant effect on Gram-negative bacteria. The TiO_2 NPs and clay showed very low antibacterial activity against both Gram-negative and Gram-positive bacteria [26].

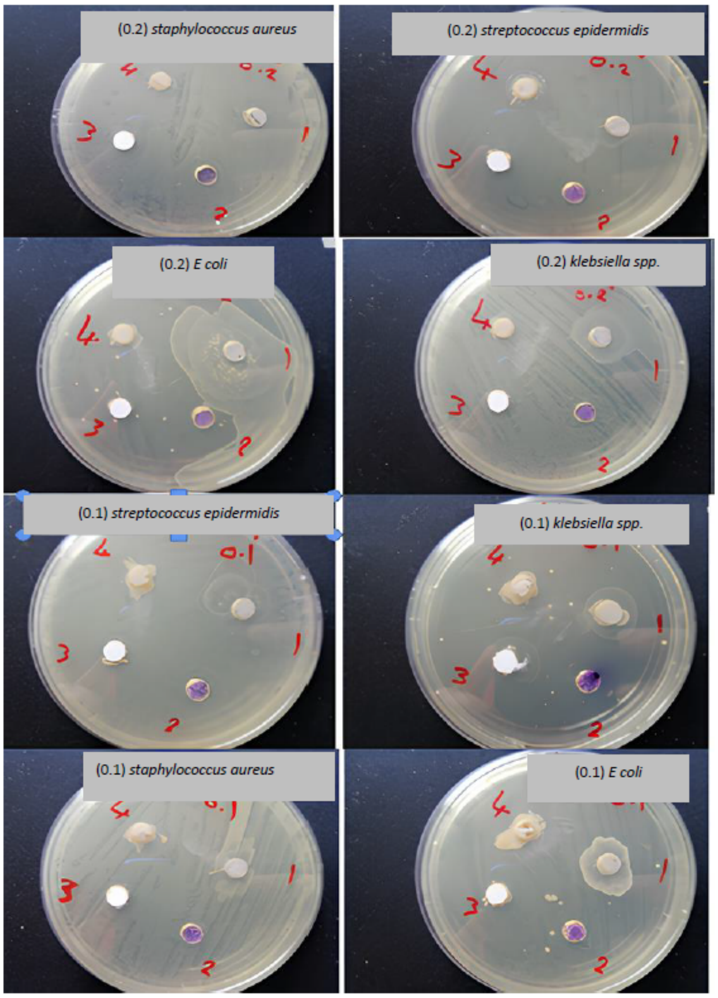

Figure 3. Comparison of the antibacterial activities of (1) NaA-Clay-TiO_2 NPs, (2) NaA-Clay, (3) TiO_2 NPs, and (4) clay, as determined by the disc diffusion method.

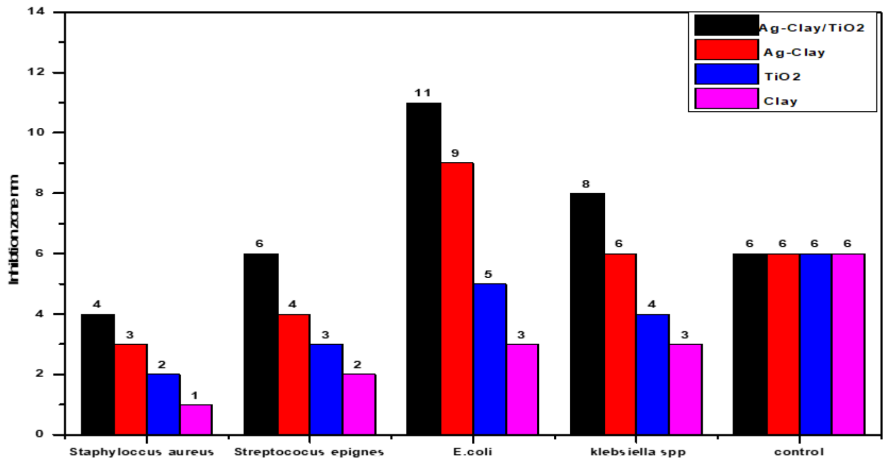

Figure 4. Inhibition zones of the four surfaces against pathogenic bacteria isolates at a concentration of 0.1 gm.

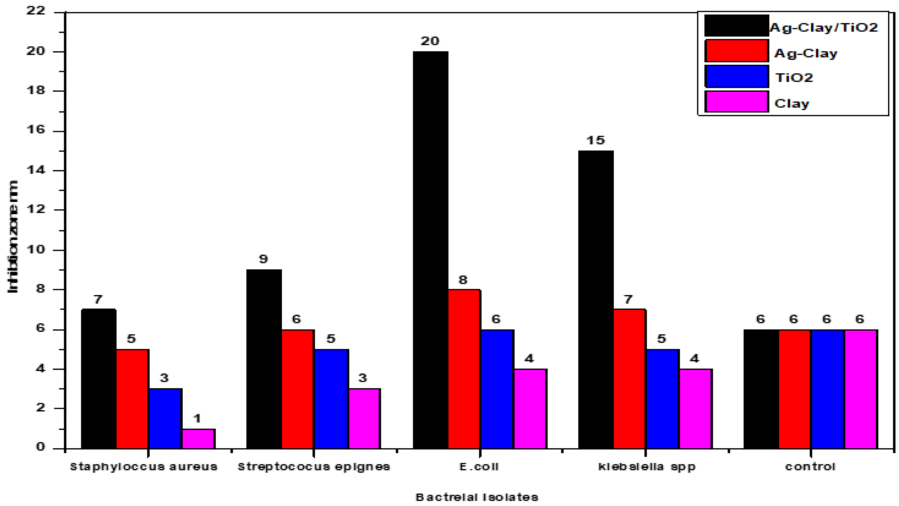

Figure 5. Inhibition zones of the four surfaces against pathogenic bacteria isolates at a concentration of 0.2 gm.

3.4. Future Scope and Generalizability

The results of this research carry substantial implications for both academic pursuits and industrial implementations. The demonstrated dual-capability of the hydrogel nanocomposite, encompassing pollutant removal and antibacterial action, posits it as a potential cornerstone in water purification technologies. The feature of regeneration and reuse further bolsters its economic feasibility and promotes a sustainable approach to resource management. The adopted methodology and consequent findings in this study present a potential paradigm for investigating other similar materials and a diverse range of pollutants. This not only expands the applicability of the research but also provides a blueprint for future exploration in the development and optimization of analogous nanocomposites for varied applications. From an industrial perspective, the hydrogel nanocomposite could potentially revolutionize wastewater treatment protocols by enhancing the removal efficiency of pollutants and bacteria. This would result in superior water quality post-treatment. Moreover, this material could be instrumental in the pharmaceutical sector, aiding in the effective removal of drug residues from generated wastewater. In essence, this study serves as a significant addition to the field of nanotechnology, laying a robust foundation for future endeavors aimed at creating efficient, sustainable materials for water treatment.

4. Conclusions

The present study demonstrated that loading titanium dioxide onto a hydrogel enhances its biological activity. Notably, the NaA-Clay/TiO_2 NPs hydrogel composite exhibited substantial antibacterial activity against the studied isolates, particularly Gram-negative bacteria. With a weight of 0.1 g and 0.2 g of the hydrogel, it presented an inhibition zone of 20 mm against *E. coli* and 15 mm against *Klebsiella* spp. at a 0.2 g weight. However, the TiO_2 NPs and clay compounds demonstrated minimal antibacterial activity against both Gram-positive and Gram-negative bacteria. Moreover, this research illustrated the potential for effective regeneration of the hydrogel nanocomposite. Remarkably, the composite demonstrated a 100% regeneration capability, allowing it to desorb in water. The adsorption process for Congo Red dye (CR), Amoxicillin (AMX), and Chlorophenol (CPH) was investigated, and successful regeneration was achieved under optimal conditions in up to four steps. These findings present promising avenues for further exploration into the potential applications of such hydrogel nanocomposites in antibacterial activity and pollutant adsorption.

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References

1. Radia, N.D.; Kamona, S.M.H.; Jasem, H.; Abass, R.R.; Izzat, S.E.; Ali, M.S.; Ghafel, S.T.; Aljeboree, A.M. Role of Hydrogel and Study of its High-Efficiency to Removal Streptomycin drug from Aqueous Solutions. *Int. J. Pharm. Qual. Assur.* **2022**, *13*, 160–163.
2. Dhiman, J.; Prasher, S.O.; ElSayed, E.; Patel, R.M.; Nzediegwu, C.; Mawof, A. Heavy metal uptake by wastewater irrigated potato plants grown on contaminated soil treated with hydrogel based amendments. *Environ. Technol. Innov.* **2020**, *19*, 100952. [CrossRef]
3. Lazaratou, C.V.; Vayenas, D.V.; Papoulis, D. The role of clays, clay minerals and clay-based materials for nitrate removal from water systems: A review. *Appl. Clay Sci. Rep.* **2020**, *185*, 105377. [CrossRef]
4. Grim, R.E.; Droste, J.B.; Bradley, W.F. *A Mixed-Layer Clay Mineral Associated with an Evaporite*; Pergamon Press, Ltd.: Oxford, UK, 1960.
5. McGraw-Hill, R.E.G. Applied Clay Mineralogy. *Science* **1962**, *136*, 870–871.
6. Saif, M. Adsorption of Brilliant Green dye from aqueous solution onto red clay. *Chem. Eng. J.* **2020**, *228*, 54–62.
7. Hoidy, W.H.; Al-Mulla, E.A.J.; Essa, S.M. Mechanical and Thermal Properties of Natural Rubber/Poly Lactic Acid/dioctadecyldimethylammonium bromide Modified Clay Nanocomposites. *J. Phys. Conf. Ser.* **2019**, *1234*, 012085. [CrossRef]
8. Anaya-Esparza, L.M.; la Mora Villagran-de, Z.; Ruvalcaba-Gómez, J.M. Use of Titanium Dioxide (TiO_2) Nano particles as reinforcement agent of polysaccharide-based materials. *Processes* **2020**, *11*, 1395. [CrossRef]
9. El Shafey, A.M.; Abdel-Latif, M.K.; Abd El-Salam, H.M. The facile synthesis of poly(acrylate/acrylamide) titanium dioxide nanocomposite for groundwater ammonia removal. *Desalin. Water Treat.* **2021**, *212*, 61–70. [CrossRef]
10. Al-Gubury, H.Y.; Fairooz, N.Y.; Aljeboree, A.M.; Alqaraguly, M.B.; ALkaim, A.F. Photcatalytic degradation n-undecane using coupled ZnO-Co_2O_3. *Int. J. Chem. Sci.* **2015**, *13*, 863–874.
11. Kangwansupamonkon, W.; Klaikaew, N.; Kiatkamjornwong, S. Green synthesis of titanium dioxide/acrylamide-based hydrogel composite, self degradation and environmental applications. *Eur. Polym. J.* **2019**, *107*, 118–131. [CrossRef]
12. Han, S.; Wang, T.; Li, B. Preparation of a hydroxyethyl titanium dioxide-carboxymethyl cellulose hydrogel cage and its effect on the removal of methylene blue. *J. Appl. Polym. Sci.* **2018**, *134*, 44925. [CrossRef]
13. Mittal, H.; Ray, S. A study on the adsorption of methylene blue onto gum ghatti/TiO_2 nanoparticles-based hydrogel nanocomposite. *Int. J. Biol. Macromol.* **2019**, *88*, 66–80. [CrossRef] [PubMed]
14. Karam, F.F.; Kadhim, M.I.; Alkaim, A.F. Optimal conditions for synthesis of 1, 4-naphthaquinone by photocatalytic oxidation of naphthalene in closed system reactor. *Int. J. Chem. Sci.* **2015**, *13*, 650–660.

15. Nizet, V. Streptococcal beta-hemolysins: Genetics and role in disease pathogenesis. *Trends Microbiol.* **2020**, *10*, 575–580. [CrossRef] [PubMed]
16. Katz, A.R.; Morens, D.M. Severe streptococcal infections in historical perspective. *Clin. Infect. Dis.* **2019**, *12*, 298–307. [CrossRef] [PubMed]
17. Al-Mashhadani, Z.I.; Aljeboree, A.M.; Radia, N.D.; Oka, A. Antibiotics Removal by Adsorption onto Eco-friendly Surface: Characterization and Kinetic Study. *Int. J. Pharm. Qual. Assur.* **2021**, *12*, 252–255.
18. Aljeboree, A.M.; Alshirifi, A.N.; Alkaim, A.F. Activated carbon (as a waste plant sources)-clay micro/nanocomposite as effective adsorbent: Process optimization for ultrasound-assisted adsorption removal of amoxicillin drug. *Plant Arch.* **2019**, *19*, 915–919.
19. Aljeboree, A.M.; Alkaim, A.F. Comparative removal of three textile dyes from aqueous solutions by adsorption: As a model (corn-cob source waste) of plants role in environmental enhancement. *Plant Arch.* **2019**, *19*, 1613–1620.
20. Bader, A.T.; Aljeboree, A.M.; Alkaim, A.F. Removal of Methyl Violet (MV) from aqueous solutions by adsorption using activated carbon from pine husks (plant waste sources). *Plant Arch.* **2019**, *19*, 898–901.
21. Aljeboree, A.M.; Hussein, F.H.; Alkaim, A.F. Adsorption and removal of textile dye (methylene blue mb) from aqueous solution by activated carbon as a model (apricot stone source waste) of plant role in environmental enhancement. *Plant Arch.* **2019**, *19*, 910–914.
22. Alkaim, A.F.; Ajobree, A.M. White marble as an alternative surface for removal of toxic dyes (Methylene blue) from Aqueous solutions. *Int. J. Adv. Sci. Technol.* **2020**, *29*, 5470–5479.
23. Hammadi, A.H.; Habeeb, S.A.; Al-Jibouri, L.F.; Hussien, F.H. Synthesis, Characterization and Biological Activity of Zinc Oxide Nanoparticles (ZnO NPs). *Syst. Rev. Pharm.* **2020**, *11*, 431–439.
24. Adam, A.M.A. Structural, thermal, morphological and biological studies of proton-transfer complexes formed from 4-aminoantipyrine with quinol and picric acid. *Spectrochim. Acta Part Mol. Biomol. Spectrosc.* **2010**, *104*, 1–13. [CrossRef] [PubMed]
25. Mundra, R.V.; Wu, X.; Sauer, J.; Dordick, J.S.; Kane, R.S. Nanotubes in biological applications. *Curr. Opin. Biotechnol.* **2014**, *28*, 25–32. [CrossRef]
26. Mukha, I.P.; Eremenko, A.M.; Smirnova, N.P.; Mikhienkova, A.I.; Korchak, G.I.; Gorchev, V.F.; Chunikhin, A.Y. Antimicrobial activity of stable silver nanoparticles of a certain size. *Appl. Biochem. Microbiol.* **2019**, *49*, 199–206. [CrossRef]

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