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Biogenic MnO_2 nanoparticles for heavy metal removal

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Abstract. This study investigates the biogenic synthesis of manganese dioxide (MnO_2) nanoparticles using aqueous extract of leek (*Allium ampeloprasum*) leaves as a natural reducing and capping agent, providing an environmentally friendly alternative to chemical synthesis. The biologically derived MnO_2 nanoparticles were applied for the removal of heavy metal ions (Pb^{2+}, Cd^{2+}, Cr^{3+}, and Ni^{2+}) from contaminated aqueous media. To enhance bioadsorption efficiency and stability, MnO_2 nanoparticles were immobilized within calcium alginate biopolymer matrices. Comparative analyses demonstrated that the entrapped nanoparticles exhibited superior biosorption performance (96–98% removal efficiency) relative to free nanoparticles or alginate alone. Adsorption equilibrium data were evaluated using the Langmuir and Freundlich isotherm models, indicating strong biosorption affinity and favorable adsorption behavior ($R^2 = 0.99861$). The results highlight the potential of green-synthesized, bio-based nanomaterials as efficient, sustainable biosorbents for heavy metal remediation and environmental protection. This approach underscores the integration of biological resources and nanotechnology for eco-compatible bioremediation strategies.

Introduction

The preservation of a sufficient quantity of water has been a crucial element in the growth of human communities. Actually, almost all water sources need to be treated in some way before they can be used for drinking [1]. Water treatment refers to the process of processing water to achieve a quality that meets the standards or criteria set by society or end users through regulatory agencies [2]. Although there are many different sources of water contamination, they can be broadly classified into two distinct groups: direct and indirect sources of pollution. Indirect sources include pollutants that get into the water supply through soil/ground water systems and rainwater that falls from the sky, direct sources involve effluent outfalls from factories, refineries, and wastewater treatment facilities [3]. Pollutants

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can be divided into two main categories: organic and inorganic [4]. when heavy metals are found in wastewater, serious environmental problem arise. It is well recognized that high levels of heavy metals are hazardous to living things. Even at very low concentrations, heavy metals can undergo bio-magnification to increase their concentration to a point where they begin to show harmful effects [5]. As a result, heavy metals are harmful to humans and aquatic life [6]. High-cost methods like precipitation, ion-exchange, membrane separation, evaporation, etc. are used for removing heavy metal ions from wastewater. These widely used methods, however, are too costly to treat wastewater with trace amounts of heavy metals [7]. Comparing nanomaterials to bulk microscale materials reveals many improved properties. The reason behind these unique characteristics is the larger surface area of them. Currently, nano adsorbent materials for wastewater treatment are made of carbon-based, magnetic, polymeric, and metal nanoparticles. Nanoparticles (NPs) with a defined shape and size are frequently synthesized via chemical and physical routes. However, these routes have been shown to be environmentally hazardous owing to the utilization of dangerous substances and elevated temperatures within the synthesis procedures. The biological synthesis of natural products is conducted by biological organisms, including bacteria, algae, fungi, and plant extracts. The biological synthesis methods of nanoparticles require further investigation. Due to the hazardous chemical's material required for synthesis, biogenic NP synthesis is an environmentally benign approach. In addition, standard temperature and pressure can be used to carry out the synthesis procedure Consequently, a growing number of scientists are directing their attention toward the biological manufacturing of nanomaterials as an alternative to those that are produced chemically or physically. A variety of biomolecules found in plant extracts, such as proteins, alkaloids, enzymes, polysaccharides, terpenoids, tannins, vitamins, phenolics, and flavonoids, can be included into the creation of nanoparticles [8]. so used a new way to adsorption heavy metals from water by nanotechnology, this research taking into account heavy metals, which regarded as inorganic contaminants, and how adsorption some types of heavy metals (Pb, Cd, Cr, Ni) that flowing from wastewater to river water and treated by MnO2 nanoparticles biosynthesis and resin of Ca-alginate.

2 Biosynthesis of MnO2 NPs Using Leek Plant Extract

Use the aqueous extract of leek leaf after it was prepared by weighing 10 grams of leaf's, washing it well with distilled water to remove dirt and dust, cutting it into small pieces, then placing it on a magnetic stirrer for an hour at a temperature of 35 °C, then filtering it, to obtaining the leek extract, and cooling it to room temperature. prepare manganese dioxide nanoparticles, 10 grams of the extract were added to 1 gram of manganese salts of manganese sulfate monohydrate (MnSO4.H2O). The mixture was subjected to a shaking incubator at30 °C overnight. Subsequently, the filtrate had been separated to the precipitate using a centrifuge at 4000 rpm to 8 minutes. The precipitate was then thoroughly washed three times using deionized water and dried at 37 °C for 6 to 8 hours. The manganese dioxide nanoparticles are ultimately milled to produce a blackish-brown powder, as illustrated in the Figure 1.

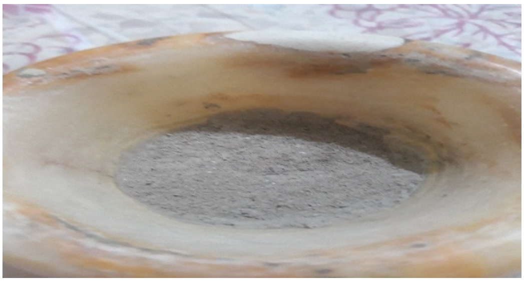

Fig.1. MnO_2 -NPs powder by biosynthesis

3 Characterization of the synthesized MnO2 nanoparticles

3.1 (UV-Vis) analysis

The Ultraviolet-visible (UV-Vis) spectral analyses are performed for MnO_2 NPs synthesized by green method from extracts of *leek* leaves. According to the UV spectra, the maximum wave length for MnO_2 nanoparticles is around 287.5 nm, and lower wave length for MnO_2 at 291 nm is consistent with previously reported data. The absorption spectra of MnO_2 NPs are given in Figure (2). the energy gap for the maximum wavelength was measured to be (4.31) eV and (4.26) eV for lower wavelength. The results of XRD and UV-Vis results are so compatible. There is an increase in the energy gap as the crystal size decreases. the energy band gap E of MnO_2 Nanoparticles was calculated by formula:

$$E= (hc/ \lambda_{max})$$

where, h = (6.626×10^{-34})Js planks constant, c= (3×10^{8}) m/s the speed of light, E: the band_ gap energy and λ_{max} is a nanoparticles wavelength.

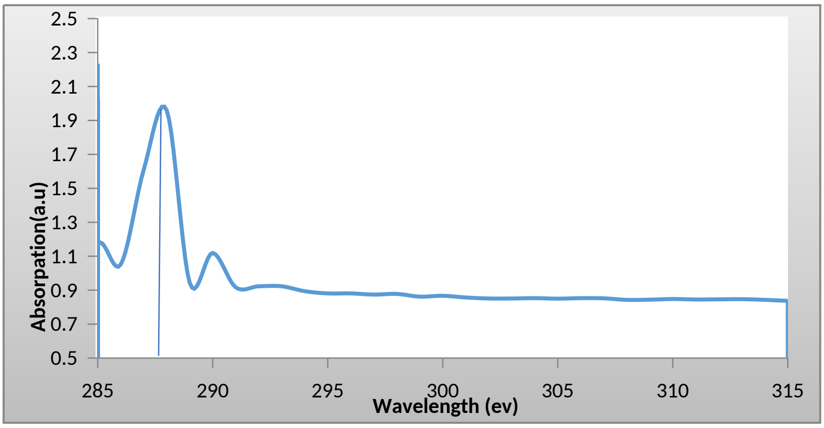

Fig.2. (UV-_Vis) spectroscopy of MnO_2 -NPs biosynthesis.

3.2 XRD analysis

X-ray diffraction patterns were acquired using Cu-Ka photons from a diffractometer (Persee, China) operated at (15-60) kV and (6-50) mA. MnO_2 compositions of biosynthesized by green method were characterized by XRD analysis patterns, which were provided in Figure (4) demonstrated the presence of peaks diffraction of MnO_2 samples matched well with (JCPDS no :44- 0141), The XRD pattern of MnO_2 NPs, is broad and has been associated with the existence of amorphous and bio-capped materials. Diffraction peaks were seen at 2θ. It is conceivable to match reflection angles of (18.2, 26.84, 38.4, 40.3, 42.6, and 50.03) degrees with a proven orthorhombic structure for MnO_2 , the highest intensity for MnO_2 NPs recorded crystalline size of (30.20) nm at (2θ) of 25.61 Deg calculate by Debye/Scherrer equation,

$$\text{Crystal size(D)} = k\lambda / \beta \cos\theta \quad \text{——} \quad (1)$$

With (X-ray)- wavelength 0.154 nm, thickness d, the diffraction angle, and constant Debye-Scherrer is 0.9.

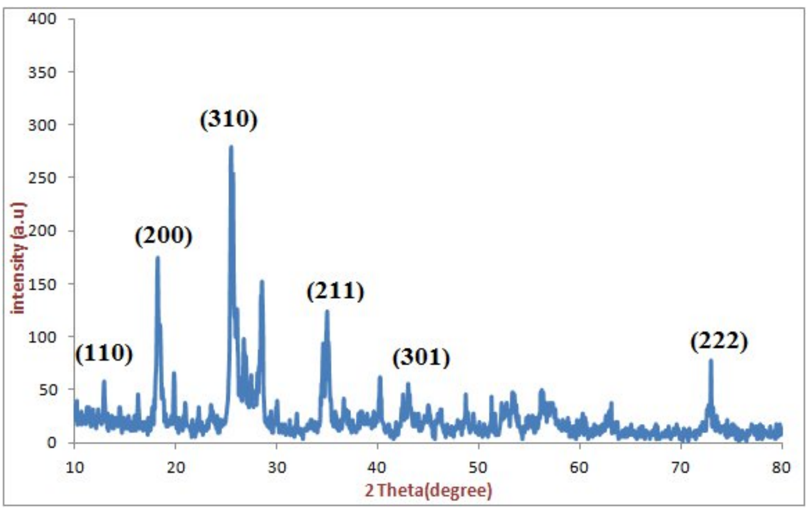

Fig.3. XRD analysis image of MnO_2 - NPs.

3.3 AFM Analysis

The concept of (AFM) atomic force microscopic gives us the ability to create topographies that show the structure of the surface. With the use of digital photographs, this technique is possible to analyze images from various angles, including 3D simulation, and to quantitatively evaluate surface properties such average-roughness (Ra) or root mean square roughness (Rq). Average grain sizes in diameter of MnO_2 NPs were (50.20). The NPs' spherical form was also shown by the morphological analysis. These AFM images show the notable adsorption of nanoparticles on the surface of the MnO_2 nanoparticle substrate [9].

4 Inorganic Contaminants of (Heavy Metals)

Heavy metal ions, including cobalt (Co), nickel (Ni), chromium (Cr), lead (Pb), and cadmium (Cd), have long been prevalent in the environment due to their toxicity to human life.. For example, Pb can produce lethargy, depression, neurologic symptoms, and thirst. These metals, in contrast to organic contaminants, do not break down into innocuous byproducts

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and are found in the waste streams of various operations [10]. Table (1) lists the maximum permissible concentration (MPC) of metals which may be present in potable water. It is evident that the acceptable concentration levels for metals are extremely low, which is indicative of the toxicity and risks these metals provide. Table (2) presents the concentration for heavy metal ions.

Table 1. Maximum amount of metals allowed in drinking water

Metal	MCL (mg/l)	
	(USEPA)	(WHO)
Lead -(Pb)	0.015	0.01
Chromium-(Cr)	0.01	0.01
Cadmium -(Cd)	0.005	0.005
Nikel -(Ni)	0.01	0.01

Table 2. Concentration of heavy metals ion(raw) of (medical city) hospital wastewater

Concentration mg/l	Heavy metal ions
0.20	Lead
0.08	Chromium
0.006	Cadmium
0.05	Nikel

5 Design of Laboratory Columns (Adsorption experiments)

The transparent glass column used for the adsorption studies, which had an internal diameter of 2.0 cm and a height of 50 cm. To guarantee a uniform distribution of influent through the adsorbent, the adsorbents (algnaite+MnO2 NPs) were restricted in the column by a glass bedding layer packing at the top and a fine Teflon (PTFE) filter (No.1) at the bottom. With a rubber stopper mounted at the top and operated by a valve in the bottom of the column, the input waste water was fed to the column. Two containers for wastewater holding capacities. The first, located at the top of a column, was utilized as a waste water feeding container with a capacity of two liters. At the base of a column, a glass beaker was utilized as a reservoir for waste water, holding one liter of water. The column was cleaned using deionized water before adsorption tests. It was loaded with prepared (MnO2 NPs, Ca-alginate, nanoparticles trapped by alginate) hospital waste water samples in each time in order to assess the adsorbent's effectiveness in treating waste water based on a number of factors, including pH level and contact time

5.1 Based column Techniques for heavy metals removal: MnO2 NPs, Ca-alginate, and MnO2 NPs trapped by Ca-alginate beads

5.1.1 MnO2 Nanoparticles column for heavy metals removal

Study the adsorption of heavy metals (Pb, Cd, Cr, Ni) by MnO2 NPs manufactured using green method after placing glass fibers at the bottom of the glass buret and then adding 1 gram of the manufactured nanoparticles with a mixture of polluted water (raw + standard) With heavy metals 100 ml, and calculate the flow rate every (3 to 5) minutes.

5.1.2 Ca-alginate (resin) column for heavy metals removal

The (entrapment material), calcium alginate. Produced by dissolving 3 grams of sodium alginate with 100 milliliters of water that was distilled in the microwave at 120 °C for 15 minutes to achieve sterilization and complete dissolution. It is then cooled to 40 °C for practical use after preparing the dissolved sodium alginate solution, it is dropped into calcium chloride solution of a concentration 0.2 M through a sterile syringe to form small beads with diameters ranging from (1- 4) mm. The beads are then stored for processing and washed with distilled water as described in Figure (4) below

Fig.4. Schematic of the laboratory experimental column

5.1.3. MnO2 Nps trapped by Ca-alginate beads column for heavy metals removal

0.1 gm of MnO2 NPs combined with A sodium alginate solution was prepared, and the mix was gently swirled for ten minutes. It was then extruded dropwise by sterile 10 ml syringe into a 0.2M CaCl2 solution to form small beads with a diameter ranging from 1 to 4 mm. The calcium alginate beads were rinsed with distilled water then kept at 4 °C. Manganese dioxide nanoparticles were detected trapped within the beads, which colored brown due to the trapping of the nanoparticles with calcium alginate, as illustrated in Figure 5.

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Fig.5. Entrapment material with MnO2 NPs by Ca- alginate beads

Figure 6 shows Fixed-Column studies were conducted utilizing a laboratory-scale column to assess the efficacy of MnO2 nanoparticles and Ca-alginate in the removal of contaminants from aqueous solutions. Porosity is determined by dividing the volume of voids by the volume of the packed bed column. The column void fraction, denoted as porosity, represents the proportion of total volume that is void and was computed using the following equation

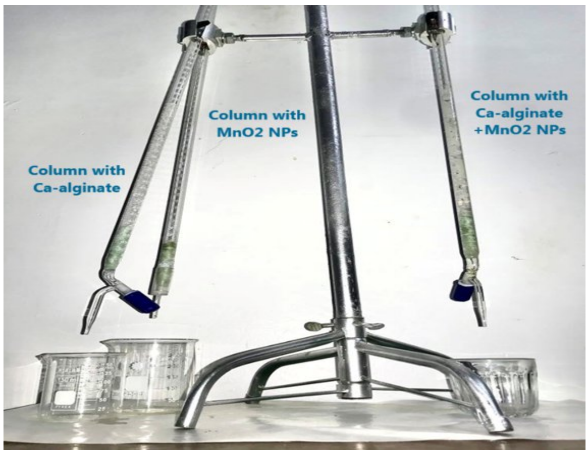

Fig.6. Schematic of the three (MnO2 NPs+ Ca- alginate, MnO2 NPs trapped by Ca- alginate) laboratory experimental column

The collected hospital wastewater samples were filtered using 0.45 μm pore filter paper as part of the wastewater treatment process, and analyzed using a flame atomic absorption spectrophotometer (Scientific Equipment Dual /Australia), to measure Concentration of heavy metals (lead- cadmium- chromium and Nickel) in the raw water and then prepare stander solution with concentration of 10 ppm in the laboratory to determine the efficiency of the synthesized MnO_2 NPs ,the resin Calcium alginate with manganese dioxide nanoparticles encapsulated in calcium alginate to eliminate and adsorb heavy metals from water. To evaluate the best extraction of heavy metals, raw water was supplemented to a concentration of 10 ppm (standard solution) for each of the following: lead, chromium, nickel, and cadmium. The treatment process is carried out by passing water contaminated with heavy metals, then the flow rates is computed every ten milliliters., and the PH value is measured before treatment, so it was between 5.5to 7.6. Regarding heavy metal contents of these samples, results exhibited that the levels of Pb, Cr, Ni, and Cd were 0.20, 0.08, 0.05, and 0.006 ppm (mg/l) respectively. after treatment the pollutant removal efficiency (R) and adsorption capacity (q) are calculated as shown in the table (3) and the removal percentage for heavy metals ions after the treatment as shown in the table (4). It is noted that the percentage of removal of heavy metals are varies, this be related to the type of treatment by MnO_2 NPs, Ca- alginate and MnO_2 NPs trapped by the resin. The removal mechanism is based on the adsorption and ion exchange. In the first column of MnO_2 NPs the heavy metals removal depends on adsorption by nanoparticles where adsorption process creates chemical or physical bonding between a porous solid media and a multicomponent fluid , providing flexibility in both design and operation together with very satisfying outcomes (adsorption efficiency)[11].The process of mass transfer known as "adsorption" occurs when contaminants in a solution are moved to a solid adsorbent. Ca-alginate (cation-exchange) resins has been studied by using columns technique. In the second column experiment, The Ca- alginate beads were added to improve that resin has good capability and efficiency for the removal of (Pb, Cr, Ni and Cd) metals from wastewater medium and the amount of resin was 30 cm. The experimental results were showed that Ca- alginate cation exchange resin is useful to recovery of Pb, Cr, Ni, and Cd has good recovery. In the third column experiment, show very good removal for heavy metals where the Ca- alginate beads with trapped MnO_2 nanoparticles was added and the results show height capability and efficiency for the removal of (Pb, Cr, Ni and Cd) metals from wastewater medium and the amount of resin was 30 cm. The experimental results were showed that the pollutant removal efficiency (R) and adsorption capacity (q) in the third column better than first and second column Thus, the municipal wastewater system would not be significantly contaminated by these harmful contaminants. Various adsorption forces, whether physical or chemical, can effectively adsorb specific pollutants [12]. Weak Van der Waals forces facilitate physical adsorption, whereas robust covalent connections between adsorbent as well as the adsorbate induce chemical adsorption. Removal effectiveness R and adsorption capacity q are computed as illustrated in the table.(5) using Equations (1) and (2) :

$R = (C_0 - Ce) \times 100/C_0$ …..(1)

$q = (C_0 - C) \times V/M$….. (2)

where C_0:(mg/L) and C:(mg/L) are the initial and final pollutant concentrations in the solution, respectively. V(L)/ is the volume of the solution, and M(g)/ is the mass of the magnetic nanoparticles [13]

Table 3. Efficiency of pollutant removal (R) following treatment with MnO2 nanoparticles, calcium, alginate, and MnO_2 nanoparticles encapsulated in calcium alginate

Concentration after removal ions by $_2$alginate MnO NPs Trapped by Ca- alginate mg/l	**Concentration after removal by Ca-alginate mg/l**	**'oncentration fter removal by MnO_2 NPs mg/l**	**andard Heavy Metals ions Concentration mg/l**	**Heavy metals ions Raw Concentration**
0.11	7.540	5.673	10	**0.20 = Pb**
0.24	8.870	4.039	10	**).08 = Cr**
0.22	7.634	4.732	10	**0.05 = Ni**
0.38	9.11	7.520	10	**).006 =Cd**

Table 4. Adsorption Capacity (q) after treatment by MnO2 NPs, Ca- alginate and MnO2 NPs trapped by Ca-alginate

Adsorption (Capacity (q After treatment by MnO_2 NPs Trapped with Ca- alginate mg/l	**Adsorptionn Capacity (q) After treatment with Ca-alginate mg/l**	**Adsorption Capacity q) After Treatment) with .(MnO_2 (mg/l**	**Standard Heavy Metals ions Concentratio n mg/l**	**Heavy metal ions Raw Concentration**
0.11	7.540	5.673	10	**0.20 = Pb**
0.24	8.870	4.039	10	**0.08 = Cr**
0.22	7.634	4.732	10	**0.05 = Ni**
0.38	9.11	7.520	10	**0.006 =Cd**

Table 5. Heavy metals ions removal concentration percentage after treatment by MnO_2 NPs, Calcium alginate and manganese dioxide nanoparticles encapsulated within calcium alginate

Heavy metals ions	Concentration removal Percentage By MnO_2 mg/l %	Concentration removal Percentage by Ca- alginate mg/l %	Concentration removal Percentage By MnO_2 +Ca-alginate mg/l %
Pb	44.38	26.07	98.92
Cr	59.93	12.00	97.61
Ni	52.91	24.03	97.81
Cd	24.84	8.954	96.20

6 Adsorption Isotherm Study

The investigation of thermal equilibrium in the adsorption process is becoming increasingly significant for comprehending the binding mechanism of dissolved solutions to adsorbents composed of granules and nanoparticles constrained by alginite granules. Consequently, this study employed two models: the Freundlich model and the Langmuir model.

6.1 Langmuir Isotherm Model

The linear equation of the Langmuir model can be expressed in the following manner, assuming that maximal adsorption occurs through the saturation of the primary layer with dissolved ions.

$Ce/Qe = Ce/Qm + 1/bQm$.................................. (1)

b is the Langmuir constant and has a relationship to the adsorption capacity (Qm), by drawing the relationship between (Ce / Qe) against CE and (Qe/1 against 1 / Ce), we obtain a linear relationship, and Langmuir constants were calculated from it. The values of these constants are shown in the table below. The treatment relationship with the restricted material and nano (R2 = 0.99861) is stronger than the relationship with the restricted material alone (R2 = 0.99735), which generally represents a good fit. The constant of the separation coefficient of the Langmuir model RL, which can be calculated from the equation RL = 1/1+bC0, was also calculated. Since Co mg / L is the highest concentration of the adsorbent solute, its value gives a good indication of the nature and form of adsorption. If its value is greater than 1, adsorption is not preferred, and adsorption is preferred if its value is between 0 and 1, through this study and applying the Langmuir model, it was found that the value of the separation coefficient constant for the first and second experiments, respectively: 0.536524 and 0.45262, which indicates that adsorption is preferred for the two systems studied.

Table 6. The thermodynamic equilibrium constants in the Langmuir equation for the bound substance with nanoparticles

Intercept	Slope	Q_m(mg/g)	b (l mg $^{-1}$)	RL	R2
0.17516	2.0277	5.709066	0.086385	0.536524	0.99861

Table 7. The thermodynamic equilibrium constants in the Langmuir equation for the bound substance with nanoparticles

Intercept	Slope	Q_m(mg/g)	b (l mg $^{-1}$)	R_L	R_2
150.315	18.178	0.05501083	0.120936	0.45262	0.99735

6.2 Model Isotherm Fruendlich

It is among the most ancient models employed for heterogeneous systems. Freundlich's linear model is represented by the following equation [14]:

$$logQe = 1\ n\ logCe + logKf$$

In this context, KF represents the Freundlich constant, indicating adsorption capacity, while N signifies a constant that reflects the intensity of adsorption. Qe denotes the adsorption capacity. Figure 3 illustrates the graphical correlation between log C and log Qe. The correlation coefficients for the experiment involving the bound nanomaterial and the bound material alone are 0.830 and 0.9932, respectively, indicating a strong linear relationship between the two variables. The constants of the Freundlich equation were derived and recorded from this equation. The constant values of the bound material with nanoparticles and the bound material serve as indicators of the adsorption capacity of this treatment

Table 8. The thermodynamic equilibrium constants in the Langmuir equation for the bound substance with nanoparticles

Intercept	Slope	n/1	K_f	^2R
0.70276	0.04215	0.04215	5.043825	0.83012

Table 9. Thermodynamic equilibrium constants of the Freundlich and Langmuir equations for adsorption of heavy metals by nanoparticles limited by CA-alginate granules

Intercept	Slope	n/1	K_f	^2R
10.09	10.7457	1.7457	1.79597	0.99322

It is concluded that the restricted material and the restricted material containing nanoparticles serve as excellent adsorbents for the removal of heavy metal ions from water, achieving removal rates of 99% for lead and 84.3% for cadmium at certain concentrations. The Langmuir isotherm binding coefficient is lower than that of the Freundlich isotherm, indicating that the latter is more appropriate for characterizing the adsorption of heavy metals on the surface of Fe_2O_3@MnO_2 nanoparticles**.**

7 The characteristic constants for the adsorption rate were determined using the Pseudo-First-order and Pseudo-Second-order models

Pseudo-first-order model

The study determined that the Pseudo First-Order model is inappropriate for this experimental data, as the graph line fails to intersect all points. The Pseudo Second-order model is appropriate for experimental data, as evidenced by the line that intersects most data points. The calculated adsorption capacity (q_e) from the model closely aligns with the practical adsorption capacity (q_e), and the value of R^2 approaches 1 (0.999). Consequently, this model is deemed suitable, as illustrated in the accompanying figures 7-8 and tables 10-13.

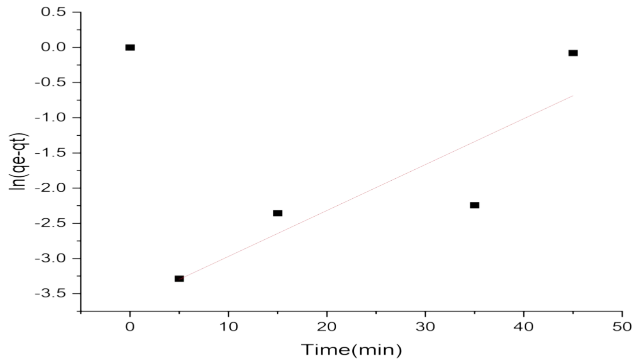

Fig.7. Pseudo First-Order Model of the First-Order Model in the Alginate Granular Material Treatment System

Table 10. Calculation of constants via the Pseudo First order model on the alginate granular matter treatment system

Intercept	Slope	(q_e(mg/g	K_f	^{2}R
3.62306-	0.06526	0.026701	0.00145	0.65581

Table 11. calculation of constants via the First-Order Pseudo First order model of the Fe2O3@MnO2 restricted nanoparticle treatment system bound with calcium alginate granules

Intercept	Slope	(q_e(mg/g	K_f	^{2}R
1.60902	0.00102	4.997911	2.266670	0.90849

Table 12. Calculation of constants via the Pseudo Second order model, First-Order model on the alginate granular restricted matter treatment system

Intercept	Slope	(q_e(mg/g	^{2}qe	${}_2$k	^{2}R
0.34926-	0.20485	1.227341	2.454682	1.16642-	0.98502

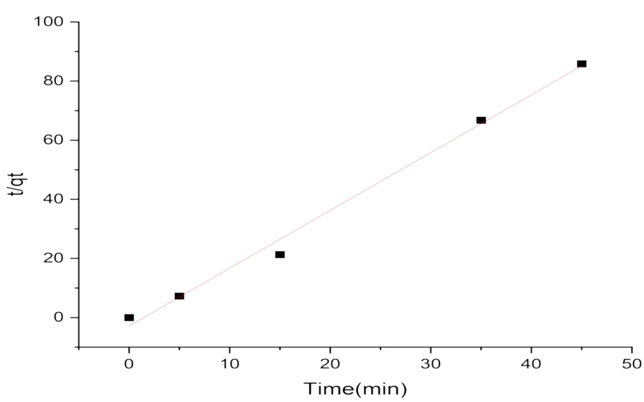

Fig.8. Pseudo first-order model of the Fe2O3@MnO2 restricted nanoprocessing system bound with calcium alginate granules

Table 13. Calculation of constants via the Pseudo Second order model, First-Order model on the alginate granular restricted matter treatment system

Intercept	Slope	(q_e(mg/g	^{2}qe	$_2$k	^{2}R
2.85254-	1.95531	7.066109	14.13222	4.95426-	0.99359

8 Conclusion and recommendation

This study examines the biological production of MnO2 nanoparticles and their efficacy as adsorbents for heavy metals in contaminated water. X-ray diffraction (XRD) validated the nano-architecture of the particles. The findings exhibited significant capacity and efficacy in eliminating metal ions (lead, chromium, nickel, and cadmium) from wastewater. Calcium alginate-entrapped nanoparticles exhibited superior pollutant removal efficacy compared to either alginate or nanoparticles in isolation. The elimination efficiency of heavy metal ions following treatment with manganese oxide nanoparticles encapsulated in calcium alginate varied from 96% to 98%. This research employed two models: the Freundlich model and the Langmuir model. The Langmuir distribution coefficient constant (RL), indicative of the maximum concentration of adsorbed solute, effectively reflects the characteristics and mechanism of adsorption. Adsorption is encouraged when its value ranges from 0 to 1. This research and application of the Langmuir model yielded distribution coefficient constants of 0.536524 and 0.45262 for the first and second experiments, respectively, demonstrating the adsorption preferences of the two systems examined.

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