The Action of Khawa Clay Nano Composite in Bacterial Treatment

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Abstract
The use of polymer nanocomposites as novel materials for water remediation has emerged as a promising alternative for disinfection of bacteria contaminated water. Sodium alginate, a natural biopolymer has been investigated in this study by encapsulating antimicrobial zinc oxide nanoparticles supported Khawa clay. The confirmation of the alginate nanocomposites was done by use of TEM, FESEM and XRD. The antimicrobial activity of khawa clay alginate nanocomposites was investigated by batch studies using wastewater outlet. The effect of Khawa clay ZNO-nanocomposite beads on total count of bacteria and count of enterobacteriacea has been studied. The inactivation results indicated that the nanocomposite effectively inactivated bacteria in wastewater. With an amount of 0.5 g of the khawa clay ,0.2 g, 0.5g,1g from nanocomposites beads, the decreased in number of bacterial count have an expulsion relationship with the increased of nano composition beads of khawa clay concentration. Development of clay-based adsorbents with high efficiency to capture bacteria from water will certainly be worthwhile due to their ready availability, low-cost and ease of preparation. Therefore, the results of this study have indicated that the alginate nanocomposites can be deemed as a potential antimicrobial agent for water disinfect. Sodium alginate immobilized microorganisms were found to be an environmentally friendly and cost-effective alternative for treatment of municipal and industrial wastewater outlet. The use of clay materials will be useful for disinfection and treatment of water and wastewater in the near future.
Keywords: khawa clay, zno-nanopartical, sodium alginat.

1. Introdaction

The presence of bacteria in water is of major concern to the global economy due to the threat they pose to humans and animal life, although water is an essential part of life, in developing countries, some communities are still largely dependent on the use of water from open sources such as rivers, streams and dams. Often times this water is not clean and safe for human consumption as it is infested with bacteria. The World Health Organisation (WHO) has reported that almost a million people die each year in developing countries, due to lack of clean drinking water (1, 2).
In this study, sodium alginate was selected as the host polymer to encapsulate ZnO-NPs loaded khawa clay to form polymernanocomposites
The Iraqi clay is one of the richest and most diverse in the region and the world because it was formed thousands of years ago in this ancient country as a result of geographical diversity from north to south. In general, the clays consist mainly of silica, aluminum and water and often also contain iron, magnesium and other alkaline elements, and constitute a large proportion It is one of the components of some sedimentary rocks such as clay and shale, which is one of the basic components of the soil, and many researchers are interested in the physical and chemical properties of the importance of this in broad areas of application such as construction engineering, ceramic industry, soil fertility, agriculture and others (3, 4).
Khawa clay is the main substance that was in common use more than a century ago and used to soften the hair of women and soften their skin. Shampoo was not known at the time. This natural substance played an important role among women in the entire Iraqi society and to define this substance, it is a type of soil that is characterized by high softness. It is free from calcareous substances that have an effect on the skin and turns easily into a very fine powder and forms with water a gelatinous colloidal solution that remains suspended throughout the water content for a long time. In addition to the high purity of this soil, it plays an important role in the maintenance of skin and hair. In order to identify this material with its scientific and technological position through the studies carried out by the Iraqi General Company for Geological Survey and Mineral Investigation, the material was found Two types with two mineral bases, either sodium or calcium, and the first is the best and has many benefits, unlike the second, which has fewer applications and can be easily converted by replacing calcium with sodium in an easy process by treating calcium-based raw bentonite with caustic soda, so it turns into the desired type and the industries in which it is used (shampoo, glass, cement, etc.). Lubricating greases, well drilling materials, fodder, paints, paper, rubber, fertilizers, pesticides and pharmaceutical industries (5).

2. Material and Method

The following instrument which used in the present study are listed in the table (1).

Table. 1 Laboratory instrument:		
No.	Instrument	Company
	Autoclave	Korea
	Sensitive Balance	Germany
	MicroWave	Germany
	Oven	Memert/Germany
	Incubater	Germany
	Centerifuge	Germany
	Magnetic Stirrer	france
	VITEK-2 Compact System	France
	Burner	Turkey
	Plain tube plastic	japan
	Loop	England
	Petri Dish,Beaker ,Cylinder ,Bottles ,Spatula ,Filter Paper , Washing Bottle	Different Origins
	Transmission electron microscopy (TEM)	China
	Field Emission Scanning electron microscopy (FESEM)	Japan
	XRD(X-ray diffraction analysis	Japan
	Fourier Transform Infrared (FTIR)Spectrometry	China
	HOTPLATE STIRRER	China
	VORTEX MIXER	China

3.5 CHEMICAL MATERIALS

Table. 2 Chemical material used in present study:		
NO.	MATERIAL	ORIGIN
	Ethanol	Thomas baker (India)
	Sulfuric acid (98%)	Thomas baker (India)
	Khawa clay	Iraq
	Cacl2	Thomas baker (India)
	Sodium alginate	Germany (sigma – aldrich)
	Zinc oxied –nano particle	American

A- Synthesis of KHawa clay supported ZnO nanoparticles

khawa clay graoundand sieved to a size <150 μm. The clay was then chemically activated by acid treatment with 3 M sulphuric acid and washed for 5 time with distilled water.

Zinc oxide nanoparticles dispersed in ethanol were calcined at 500 C for 5 h to obtain the powdered nanoparticles.

Khawa clay supported ZnO-NPs was obtained by weighing (0.1g) of the nanoparticles into 0.5 g of the acid activated clay and heated under reflux at 60 C for 20 min in a microwave at a power setting of 500 W. The resulting suspension was filtered and washed 4 time with distilled water.

The clay composite was then dried on filter papear overnight in air at 60 C and after crushed and sieved to 150mm for later use.

B - Synthesis of ZNO_KHawa clay nanocomposites encapsulated alginate beads

The alginate solution was prepared by dissolving 3 g sodium alginate salt into 300 ml distilled water and stirred thoroughly until a clear solution was obtained. On the other hand 0.5g from ZNO KHawa clay nanocomposite was added in to 5ml distilled water and stirred.

Added 10ml from alginate solution to ZNOKHawa clay solution and 15ml from alginate solution to ZNOKHawa clay solution and 20 ml from alginate solution to ZNOKHawa clay nanocomposite and 25ml from alginate solution to ZNOKHawa clay nanocomposite solution.

Each two solutions were then mixed together and stirred to obtain a homogeneous dispersion. The resulting alginate dispersion was extruded using a peristaltic pump into the gelation medium.

The gelation medium was 0.2 M CaCl2. The extrusion was done under slow stirring to improve the bead formation and also to prevent the aggregation of the formed beads. The formed alginate beads were then left in the solution for 10 min. Afterwards, the CaCl2 solution was decanted, and the beads washed several times with water and then freeze-dried for 3 days.

C. Antibacterial studies

1- To determine the antibacterial activity of the KHawa clay and KHawacly alginate nanocomposites, wastewater contain bacteria was investigated through batch experiments. (1ml) of waste water sample after maked second dilution was pipetted into center of 3 empty petri dishes and about 20 ml of nutrient, blood and macconkey agar were poured on the samples, after that the petri dishes were rotate clockwise and anticlockwise to spread the samples throughout the agar and allowed for about 5 minutes to solidify ,then petri dishes were inverted before incubation . these dishes incubated at 37 C for 24 h. where nanoparticles stayed 24h in waste water for treatment. According to (6) the number of colony was determined N= N1-N2/N1 where N1 and N2 number of colony before and after treatment .

The following table for different Weight of bentonite zno nanocomposites beads and khawaclay zno nanocomposites beads:

Table.3 Alginate Concentration and weight beads		
Alginate Concentration	Khawaclay zno beads	bentonite zno beads
10 ml	(0.2 g, 0. 5g, 1g)	(0.2 g, 0. 5g, 1g)
15 ml	(0.2 g, 0. 5g, 1g)	(0.2 g, 0. 5g, 1g)
20 ml	(0.2 g, 0. 5g, 1g)	(0.2 g, 0. 5g, 1g)
25 ml	(0.2 g, 0. 5g, 1g)	(0.2 g, 0. 5g, 1g)

2 - Sterilized bottles were filled with 50 ml of the waste water and the alginate nanocomposites were added. To evaluate the minimum amount of the nanocomposites that will be required to inactivate the bacteria, the nanocomposites were weighed in 0.2 g, 0.5 g and 1.0 g.

3-The sampel culture on nutrient, blood and macconkey ager before and after treatment with khawaclay and khawaclay zno nanocomposites beads with different concentration with different weight and incubat before and after treatment at 37c for 24h.

3.9. Characterization of the alginate n anocomposite

The morphology of ZnO-NPs ,ZNO Khawaclay nanocomposite was investigated by TEM instrument, operated at 200 kV.

2-The crystallinity of the samples was determined by X-ray diffraction

3- The surface morphology and dispersion of Zno

Khawaclay
nanocomposites in the alginate matrix was analysed using FE SEM.
4-KHawaclay analysed using FTIR.

3. Results and Discussion

The total count of bacteria before treatment was 4200 cfu/ml, and the removal efficiency for Khawa clay, in the form of alginate ZNO- nanocomposites beads, used different whight(0.2 g,0.5 g , 1 g). the removal efficiency for 0.2 g from beads was(18%, 35%, 45 and 57%) for the concentrations from sodium alginate(10, 15, 20, and 25), respectively, and with the same concentrations, the removal efficiency for (0.5 g) from beads Khawa clay ZNO- Nanocomposite (44%, 56%, 69%, 72%) with the same concentration from sodium alginate and the removal efficiency for (1 g) from beads of Khawa clay ZNO- nanocomposite(66%, 74%, 93%, 95%).
The following figure shows the removal efficiency of the total count from beads of Khawa clay ZNO- nanocomposite:

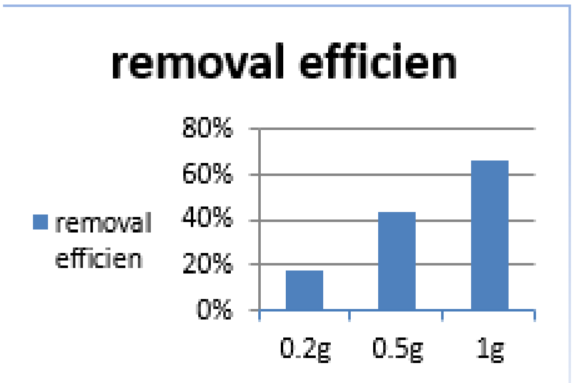

Figure 1 The percentage of removal efficiency of khawa clay- zno nanocomposidte beads in 10 ml - alginate

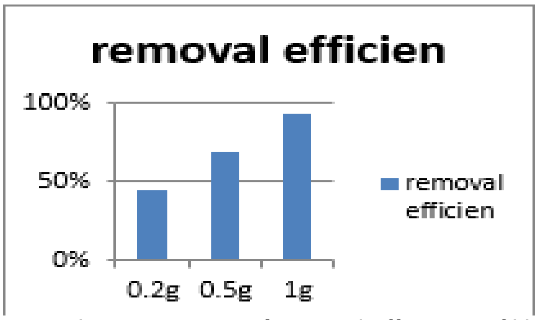

Figure 2 The percentage of removal efficiency of khawa clay- zno nanocomposidte beads in 20 ml - alginate

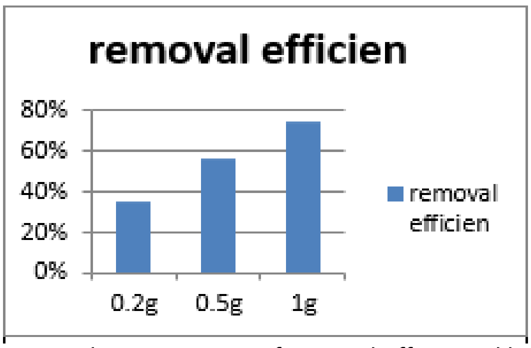

Figure 3 The percentage of removal efficiency khawa clay - zno nanocomposidte beads in 15 ml - alginate

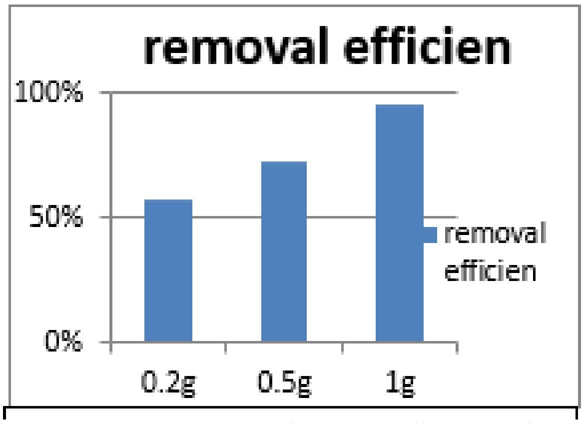

Figure 4 The percentage of removal efficiency of khawa clay- zno nanocomposidte beads in 25 ml - alginate

The number of Enterobacteriaceae before treatment wasm(2800 cfu/ml), and the removal efficiency of the Khawa clay ZNO- nanocomposite beads , , used different whight(0.2 g, 0.5 g, 1 g). the removal efficiency for (0.2g) from beads was(21%, 22%, 31%, 42%) for the concentrations of sodium alginate(10, 15, 20, 25), respectively, and with the same concentrations, the removal efficiency for(0.5 g) from beads of Khawa clay ZNO- nanocomposite with the same concentration of sodium alginate (35%, 41%, 61%, 65%) and the removal efficiency for(1 g) from beads of Khawa clay ZNO- nanocomposite(66%,70%, 89%, 97%)
The following figure shows the percentage of removal efficiency of Enterobacteriaceae Count for Khawa clay ZNO- nanocomposite:

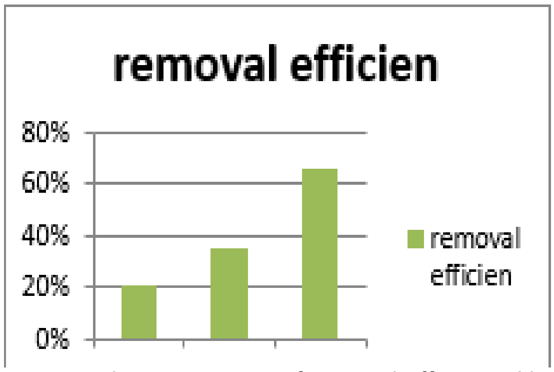

Figure 5 The percentage of removal efficiency khawa clay - zno nanocomposidte beads in 10 ml - alginate

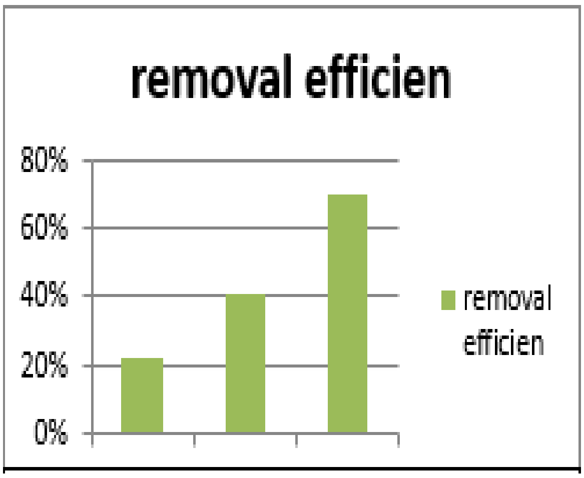

Figure 6 The percentage of removal efficiency khawa clay - zno nanocomposidte beads in 10 ml - alginate

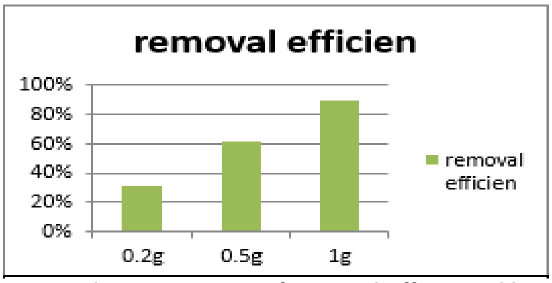

Figure 7 The percentage of removal efficiency khawa clay - zno nanocomposidte beads in 20 ml - alginate

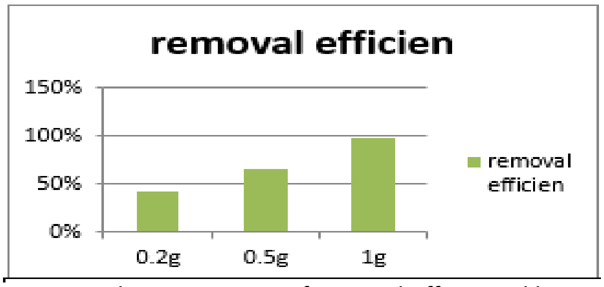

Figure 8The percentage of removal efficiency khawa clay - zno nanocomposidte beads in 25 ml - alginate

* The microbiological analyses of wastewater were performed at end of treatment. the results of bacterial profile diagnosis showed that treated water was still polluted with different type of G+ve bacteria included (Staphylococcus pseudintermedius and Staphylococcus heamolyticus and Kocuria varians) and G-ve bacteria included(Pseudomonas aeruginosa , Escherichia coli, Enterobacter aerogenes and, Enterococcus faecalis) all these bacterial species were diagnosis phenotypically in different culture like MacConkey , Blood , Nutrient and chromogenic agar , and then confirmed by VITEK- 2 system as follows :

- Bionumber : 0405610450402610 (Escherichia coli).
- Bionumber : 0405610550506610 (Escherichia coli).
- Bionumber : 0405211544500600 (Escherichia coli).
- Bionumber : 0405610550506610 (Escherichia coli).
- Bionumber : 0405610550524610 (Escherichia coli).
- Bionumber : 6627734553577010 (Enterobacter aerogenes).
- Bionumber : 156002765773771 (Enterococcus faecalis).
- Bionumber : 010006043760231 (Staphylococcus heamolyticus).
- Bionumber : 01041217363231 (Staphylococcus pseudintermedius).
- Bionumber : 0003453103500252 (Pseudomonas aeruginosa).
- Bionumber : 014000140000030 (Kocuria varians).

The obtained results recorded evealed that a significant decrease in the densities of bacterial indicators counts included Total viable counts and Enterobacteriaceae viable counts and increased in bacterial removal rate by using nano composition beads of khawa clay in different weight and the decreased in number of bacterial count have an expulsion relationship with the increased of nano composition beads of khawa clay weight As shown in the figures above.

Water pollution is the major problem in the global surrounding. And it is major causes of illness and mortality worldwide (7). Now the awareness for the disposal of industrial wastewater, pretreatment and proper purification of water is the prime responsibility of all the people around the globe. Many laws, policies and a lot of technological advancement have been made related to recycling of industrial water and/or its treatment before it is discharged into the environment.

People are responsible for causing the water pollution on this earth. This water pollution is the results of using different types of chemicals used in agricultural sector (such as herbicides, pesticides, fertilizers), use of detergents and soaps by human being in daily life, and major pollution is cause by industrial sectors (such as textiles, electroplating, mining and other chemical industries) which released highly toxic chemicals (8).

Wastewater treatments are processes in which microorganisms play crucial roles and illustrate well some of the principles of biogeochemistry. Wastewaters are materials derived from domestic sewage or industrial processes, which for reasons of public health and for recreational, economic, and aesthetic considerations cannot be disposed of merely by discarding them untreated into convenient lakes or streams.

Rather, the undesirable and toxic materials in the water must first be either removed or rendered harmless. Inorganic materials such as clay, silt, and other debris are removed by mechanical and chemical methods, and microorganisms participate only casually or not at all. If the material to be removed is organic in nature, however, treatment usually involves the activities of microorganisms, which oxidize and convert the organic matter to CO2. Wastewater treatment usually also results in the elimination of pathogenic microorganisms, thus preventing these organisms from getting into rivers or other supply sources. As a result of the sewage treatment process, the effluent is stabilized and its content of toxic materials is reduced, it can thus be disposed into the environment with less difficulty. (9) recorded that total and faecal coliforms were around 107 in marine water mixed with raw sewage. (10) found that faecal coliform in the raw wastewater was 3.9 x 107 as mean value. (11) reported that faecal streptococci counts in raw wastewater were around 106 to count /100ml either under warm or cold conditions.

1. Fourier transform infrared spectroscopy (FTIR) analysis

FTIR analysis is an effective tool for characterizing functional groups in organic and inorganic compounds in the range of 400-4000 cm^{-1}. Figure (9) shows the FTIR spectrum of the khawa clay, as it was observed that absorption bands appeared at 3695 and 3658 cm^{-1}, due to the symmetric and asymmetric stretching vibration of hydroxyl groups (Al-OH-Mg). The absorption band at 3622 cm^{-1} was due to the Al-Al-OH stretching vibration and H_2O molecules present in the sample.

Low-intensity absorption bands appearing at 2934, 2856 and 2370 cm^{-1} are due to overtones and combination tones of SiO_4 and the absorption of CO_2 molecules (12). The wide absorption band at 1637 cm^{-1} is due to the H-O-H bending vibration, and this confirms that water is an essential part of the mineral composition. Sharp and high-intensity absorption bands at 1107 and 1035 cm^{-1} are due to the stretching vibration of the Si-O bonds of the tetrahedral sheets. In contrast, the absorption bands appearing at 914, 754, and 692 cm^{-1} are due to OH (Al-Al-OH), (Al, Mg)-OH, and Si-O-Mg bending vibrations, respectively. Finally, the absorption bands at 538, 468, and 424 cm^{-1} are due to Si-O-Al and Si-O-Si bending vibrations (13,14).

Table4. FTIR characterization of khawa clay (bentonite)		
Peak Number	Wavenumber (cm^{-1})	Functional group
1,2	3695, 3658	Al-OH-Mg
3	3622	Al-Al-OH
4,5	2934, 2856	SiO_4
6	2370	CO_2
7	1637	H-O-H
8,9	1107, 1035	Si-O
10	914	OH (Al-Al-OH)
11	754	(Al, Mg)-OH
12	692	Si-O-Mg
13	538	Si-O-Al
14,15	468, 424	Si-O-Si

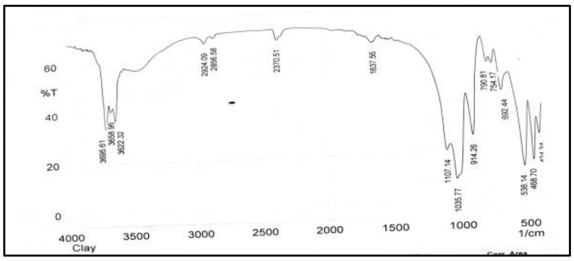

Figure 9: (FTIR) analysis

, XRD analysis was performed on Khawa clay and ZnO- khawa clay nanocomposite to identify the crystalline shape and compare it with bentonite clay. It was observed that sharp and high-intensity diffraction peaks appeared in XRD spectrum of the khawa clay at 2θ = 12.1o, 20.0o, 24.8o, 26.4o, 34.9o, 38.3o, 45.1o, 50.0o, 54.9o and 62.1o assigned to (001), (004), (012), (101), (123), (100), (101), (222), (116), and (134) planes, respectively. This indicates an increase in the crystalline character and the facility of attachment of ZnO NPs with silica inter the clay layers. After the reaction of the khawa clay with ZnO, the diffraction peaks of the clay were weakened as shown in Figure (9). The peaks of the nanocomposite at 2θ = 12.0o, 19.9o, 24.6o, 26.2o, 45.3o, 49.76, 55.0o, 58.3o and 59.6o assigned to (001), (004), (012), (101), (123), (222), (116), (124), and (200) planes, respectively are due to the presence of khawa clay. Also, the peaks at 2θ = 34.5o, 35.9o, 38.1o, 47.3o, 56.2o, 62.0o and 67.6o assigned to (100), (002), (101), (110), (103), (200), and (112) planes, respectively, confirm the presence of ZnO nanocrystal. The obtained data indicate the success of mixing khawa clay with ZnO. Finally, it was found that the average crystal size of the khawa clay and the nanocomposite are 13.3 nm and 14.7 nm, respectively

Table5. XRD data of khawa clay and ZnO- khawa clay nanocomposite					
Sample	2θ	FWHM	Intensity (I/I_o) %	d-spacing (A_o)	Crystal size (nm)
khawa clay	12.17	0.519	77.6	0.726	15
	20.02	0.792	89.5	20.023	10
	24.83	0.499	100	24.835	16
	26.47	0.363	40.1	26.479	23
	34.90	0.95	81.7	0.256	8
	38.39	0.863	86.9	0.234	9
	45.71	0.840	32.6	0.198	10
	50.09	0.58	14.3	0.181	15
	54.98	1.090	53.9	0.166	8
	62.18	0.492	47.6	0.149	19
ZnO- khawa clay	12.00	0.823	93.9	0.736	9
	19.97	0.917	90.8	0.444	12
	24.62	0.640	75.9	0.361	13
	26.26	0.344	100	0.339	24
	34.58	0.769	72.0	0.259	10
	35.90	0.558	83.0	0.249	15
	38.19	0.899	61.7	0.235	13
	45.34	0.828	28.8	0.199	10
	47.36	0.85	24.2	0.191	10
	49.76	0.44	31.2	0.183	20
	55.00	1.615	31.7	0.166	14
	56.27	0.513	25.2	0.163	17
	58.32	0.505	15.8	0.158	18
	59.69	0.559	27.4	0.154	16
	62.05	0.820	53.3	0.149	11
	67.67	0.505	30.6	0.138	24

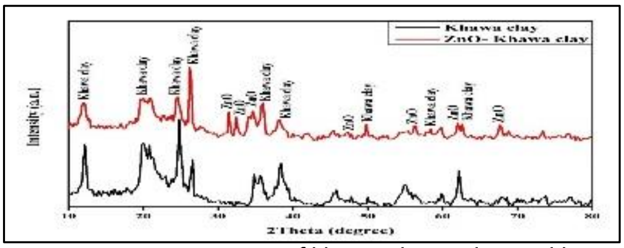

Figure 10. XRD patterns of khawa clay and ZnO- khawa clay nanocomposite

the FESEM images of the ZnO- khawa clay nanocomposite before treatment showed the presence of heterogeneous spherical shapes distributed on the surface of the zigzag grooves as shown in the Figure (10). This indicates the deposition of the bentonite clay surface by ZnO nanoparticles. Figure (11) represents the FESEM images of the ZnO- khawa clay nanocomposite after treatment with different magnifications. It was found that spherical shapes increased in size and uniformity of their distribution over all active surface sites. Therefore, the surface shape

hanges and the increase in the accumulation rate of nanoparticles confirm the successful attachment of the prepared nanocomposite with bacteria (15). Finally, the average particle size calculated by FESEM image for the ZnO- khawa clay nanocomposite before and after treatment are 68.04 nm and 87.28 nm

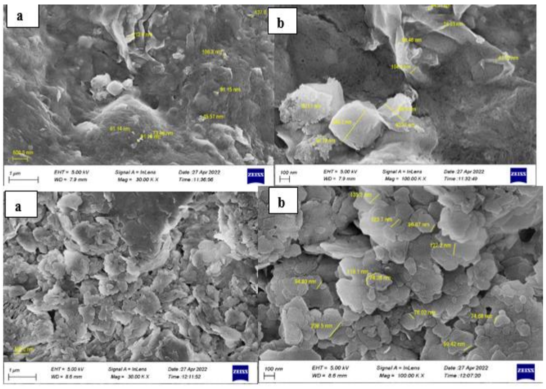

Figure 11. FESEM image of ZnO- khawa clay nanocomposite after treatment at different magnifications (a) 100 nm and (b) 1 μm khawa clay

4. Conclusion

Khawa clay alginate nanocomposites were prepared and characterized to develop a new antimicrobial material for the disinfection of water. The alginate nanocomposites encapsulated with antimicrobial ZnO-NPs demonstrated its inhibition of bacteria activity with wastewater outlet. the nanocomposites showed excellent antimicrobial activity within 24 hours by inactivating a large number of the enterobacterobacteriaceae. However, the nanocomposites showed good results after24 hour by inactivating a large number of the total count from bacteria. The inactivation was improved with more nanocomposite amount and contact time. Furthermore, the overall performance of the nanocomposites in the study shows that the nanocomposites are promising as an alternative disinfectant material for contaminated water. In addition, the cost implication for the preparation of the nanocomposites allows for a large-scale production which is good for point-of-use. This treatment is considered environmentally friendly because no reaction by-products were found. It is therefore proposed as an efficient, simple, and economical treatment that can be adopted as an alternative for wastewater treatment.

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