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The Effect of Modified Magnetic Mesoporous Silica Nanoparticles on Water Disinfection

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Abstract

In this study modified magnetic mesoporous silica nanoparticles were used for water disinfection. The pure water was contaminated artificially and the performance of these nanoparticles was investigated. Also, factors affecting the microbial contamination were experimentally set and their effects on this process were examined. Parameters such as pH, temperature, exposure time and water mass flow rate were tuned separately and the effect of each factor with and without other parameters was investigated. The experiments were done by continuous phase method and disinfection criterion was based on the measuring factor MPN. Efficiency of disinfection process was calculated using Chick-Watson law and logN/No-CT curve was drawn. The obtained results are used for drinking water purification and can be applied in the industrial refineries, too.

Introduction

Contamination refers to the introduction of materials or energy (such as heat) by human in the environment such that it threats the vital resources or human health, animals and plants. The presence of materials or energy in certain ranges in the environment is permitted and sometimes desired. Contamination occurs if these ranges increase considerably and as a result this increase can disturb the present phenomena.

Drinking water is usually disinfected and sterilized water is used only for medical and pharmaceutical applications. Water taken from lakes, rivers, streams and wetlands may appear clean and clear and have pleasant taste and odor. Unfortunately, pathogens found in water are not only harmful but also unobservable with unarmed eye. At the same time they may have no taste or smell. These bacteria, viruses and protozoa may cause nausea or fever or lead to more serious illnesses such as severe diarrhea, hepatitis A, and typhoid fever. These waters should be disinfected before use for drinking or cooking. Depending on the water resources, its use conditions, and levels of microbial contaminants, disinfection is done in short time or continuously.

The modified magnetic mesoporous silica nanoparticles have better antimicrobial property than other nanoparticles due to the larger surface area which results in more contact with microorganisms. Nanoparticles attach to the bacterial cell membrane and penetrate into it. Because bacterial membrane has proteins containing sulfur, nanoparticles interact with the cell proteins containing sulfur compounds such as DNA.

When modified magnetic mesoporous silica nanoparticles penetrate into the bacterial cell, a low molecular weight area is formed in the center of the bacterial cell. Therefore, bacterium shrinks itself to protect DNA from the modified magnetic mesoporous silica ions. In this case, nanoparticles attack the respiratory system of bacterium and resultant disturbances causes the death of bacterial cell. On the other hand, nanoparticles release the modified magnetic mesoporous silica ions and this in turn improves their bactericidal activity [1].

Comparing the impacts of the silver ions on two investigated microorganism, researchers proposed a possible mechanism for silver ions [2-6]: Silver ions penetrate into the bacterial cell through the cell wall and then convert the DNA into a condensed form. Finally, this results in the bacterial cell death. Silver ions disturb the transcription process, too. Synthesis and antimicrobial activity of silver complexes were investigated by histidine and tryptophan. 0.05m histidine and 0.05m tryptophan were added to the aqueous solution of silver nitrate to produce white sediment.

The precipitate was centrifuged and dried to evaluate its antimicrobial activity by continuous dilution. In addition, Toxicity of these complexes was tested on a group of mongrel laboratory mice. Silve-Histidine complex showed better antimicrobial activity against Gram-negative bacteria.

Baker (2014) reported the synthesis of nanoparticles by introducing an inert gas and liquefaction and quasi-liquefaction techniques. In his study, baker investigated the antimicrobial performance of nanoparticles for E.coli in a solid medium. He observed that nanoparticles show their antibacterial activity in low concentrations such that their toxic effect on E.coli cells was in concentration of $8 \mu g/cm^2$. So it is assumed that the antibacterial mechanism of silver nanoparticles is related to the ratio of their

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high surface area. Because of their larger ratio of surface area to volume, smaller particles have more effective antibacterial activity. Therefore, nanoparticles are known as the affecting toxic material on the E.coli cells.

Manka (2005) investigated the antibacterial effectiveness of silver ions for E. coli as a model organism using energy-filtered TEM systems, two-dimensional electrophoresis (2-DE), the time of flight spectroscopy along with the matrix assisted laser desorption ionization (MALDI-Tofms) [8].

According to the obtained results, silver ions penetrate into the bacterium cells than the cell membrane. 2-DE and MALDI-Tofms show that ribosomal proteins and a series of enzymes and proteins are affected by silver ions.

Researchers found that the bactericidal property of silver ions originates from the interaction of silver ions with ribosome and negation of the effect of required enzymes and proteins for producing ATP.

Malakootian et al.[9] prepared the zero-valent iron nanoparticles from boron-sodium hydroxide and chloroma with the ratio of 1:3. They investigated parameters such as pH(4,6,8,10), exposure time(5,10,15,20,65)in min , concentration of iron nanoparticles $\frac{g}{\ell}$ (10,15,…,60) and nitrate concentration $\frac{mg}{\ell}$ (25,35,50,75,…,500) and determined absorption and reaction dynamics of nitrate in terms of the most common isotherms and kinetics of adsorption.

The maximum valence of nitrate under the influence of iron nanoparticles concentration of 15g/l with the initial nitrate concentration of 50g/l was 70%, 95%, 99% and 90% at PH4 and exposure time of 60 minutes. Frendlich and Longmire isotherms are in good agreement with the obtained data. Kinetic analysis showed that nitrate uptake by zero-valent iron nanoparticles is according to the second-order kinetics. The results showed that as pH decreases and exposure time increases, the nitrate removal also increases. As the nanoparticle concentration increases, the removal percent also increases. So, the optimal conditions should be determined for more removal of nitrate.

Experimental

Preparation of Adsorbent

Synthesis of Nanoparticles

The FT-IR spectrum of Fe_3O_4-MCM-41 is shown in figure 1.a. Peaks cm^{-1} 781, 957 cm^{-1} and 1078 cm^{-1} are corresponding to Si-OH vibrations, Symmetric and asymmetric stretching of Si-O-Si, respectively. Additionally, a broad peak between 3000-3600 is related to the stretching of OH. The absorption band of Fe-O is 500-600 cm^{-1}.

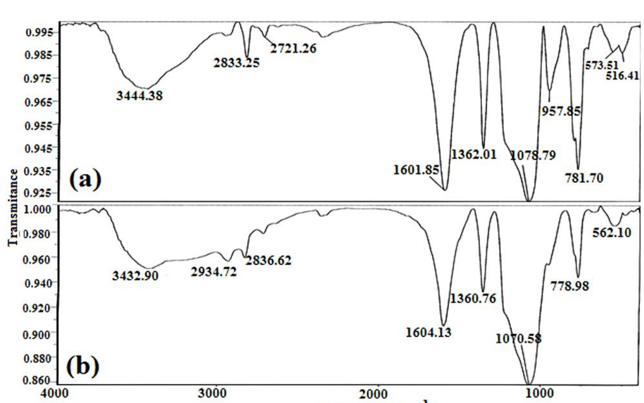

Figure 1: FT-IR spectrum (a) Fe_3O_4-MCM-41 nanoparticles, (b) Fe_3O_4-MCM-41-NH_2 nanoparticles.

Figure 1.b shows the symmetric and asymmetric stretching of methyl group in the structure of functionalized compound Fe_3O_4-MCM-41-NH_2 as a wide peak between cm^{-1} 2800-3000which is corresponding to the functional group of the porous adsorbent, i.e., amine. Moreover, a broad peak between cm^{-1} 3200-3400 is observed for the stretching of NH in amine group.

Figure 2 shows the SEM image of Fe_3O_4-MCM-41-NH_2. As seen from the figure, Fe_3O_4-MCM-41-NH_2 has a spherical topology. According to the estimation results, most nanoparticles have diameters less than 200 nm.

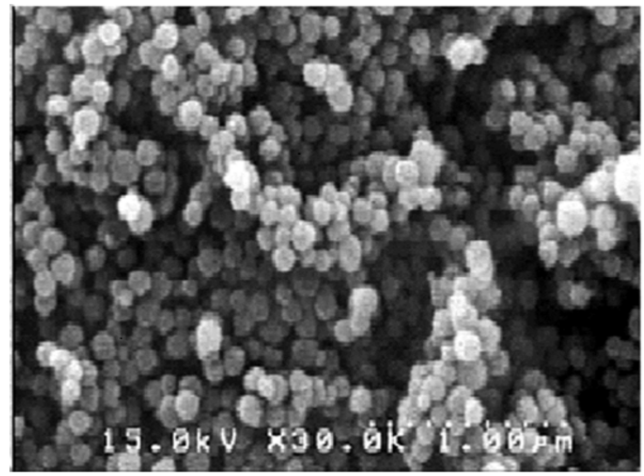

Figure 2: SEM image of Fe_3O_4-MCM-41-NH_2.

Sampling Methods

Mixed Sampling

Mixed sampling method is used to collect a mixed sample from a particular place such that the sample segments are collected in different time intervals. The mixed sample may form by collecting water from different parts of a source or from various places in different times. Figure 3 shows the scheme of the experimental set-up(Flow) used in the study.

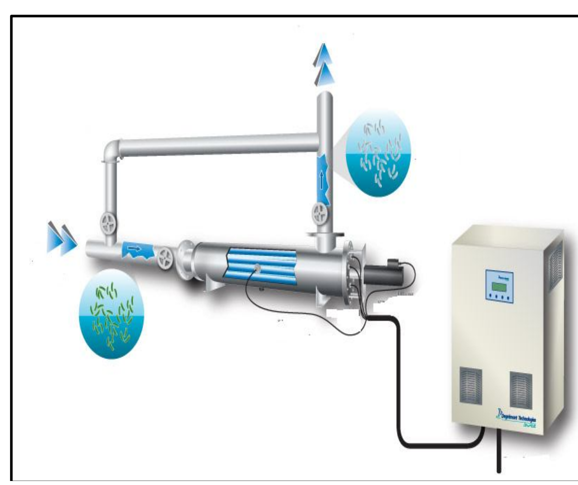

Figure 3: The experimental set-up, Flow.

The modified magnetic mesoporous silica nanoparticles were used in all disinfection experiments. These experiments were done in the continuous phase condition. A certain amount of the adsorbent was weighted and transferred into the bed and then mixed with a magnetic mixer. After a certain time, the mixed water sample is filtered and sent to the laboratory to determine MPN.

Once the respective analyses were done, the disinfection efficiency is obtained.

Results and Discussion

Investigation of the Disinfection Experiments

The Effect of PH, adsorbent amount and mass flow rate of water

pH is one of the most important parameters of disinfection. Intestinal bacteria endure more pH levels, basic and acidic environments than animal parasites. These bacteria can be activated only after bearing the gastric acidity and basic property of the bile in the intestine. These bacteria cannot bear the acidic conditions and their removal speed is high. Figures 4-6 show that as Ph decreases, absorption also increases such that absorption is 99.95% at pH=8. As seen from these figures, the adsorbent amount is other important parameter. As adsorbent amount increases, the absorption increases, too. Increased mass flow rate decreases the exposure time of water with the adsorbent, reducing the absorption level.

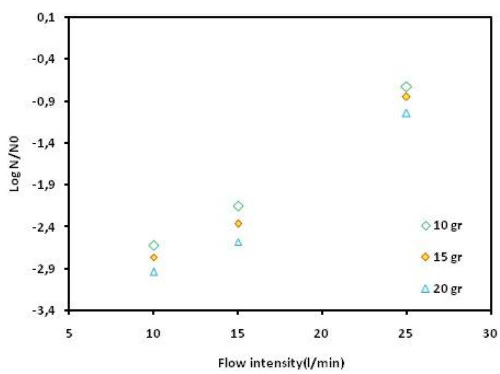

Figure 4: the effect of absorption and mass flow rate of water at Ph=8.

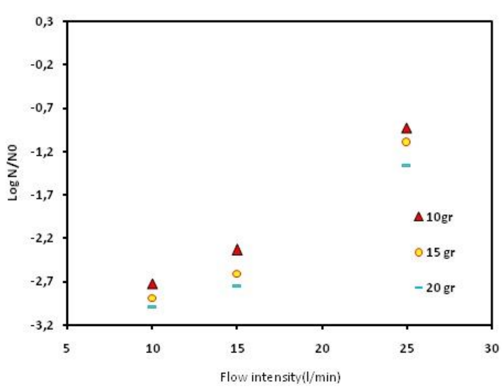

Figure 5: The effect of adsorbent amount and mass flow rate of water at Ph=10.

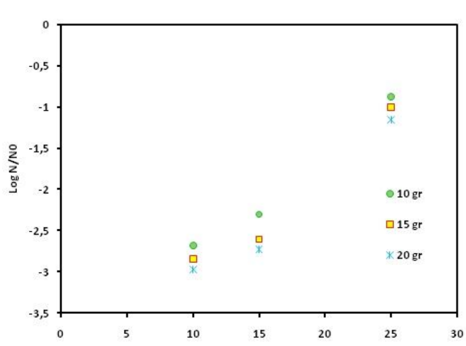

Figure 6: The effect of absorption and mass flow rate of water at pH=9.

According to the above discussions, Ph=8 was used as a basis in the next experiment. Contact time is one of the most important parameters in the disinfection process. When adding a disinfectant, its contact time with the liquid is very important. Disinfection reactors with specific physical design can provide the enough contact time. In a certain concentration of the disinfectant, long contact time can result in the more elimination of contaminants, which is given by:

$$\frac{dN}{dt} = -KNt \qquad (1)$$

Where *dN/dt* is the change in the number of organisms over time, K is the inactivation coefficient of T-1 and Nt is the organisms number in time of t. t refers to time. If N is the number of organisms in t=0, the equation is written as

$$\ln\frac{N_t}{N_0} = -Kt \qquad (2)$$

So the inactivation coefficient can be calculated by plotting $-\ln\frac{N_t}{N_0}$ v.s.t.

As seen from figures 7 and 8, as t increases, the adsorption level also increases. The inactivation coefficients of 10gr and 15 gr of the adsorbent are 0.045 and 0.0528, respectively.

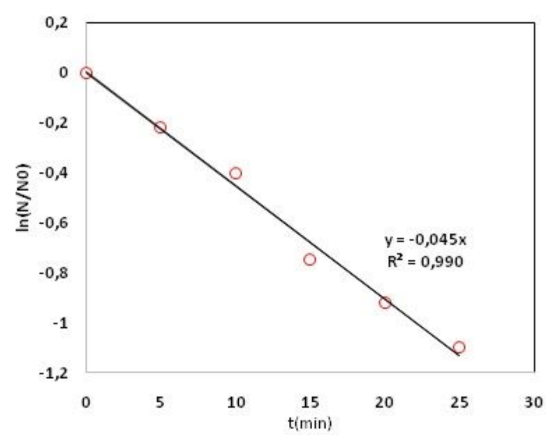

Figure 7: The effect of residual time on the absorption for 10gr adsorbent.

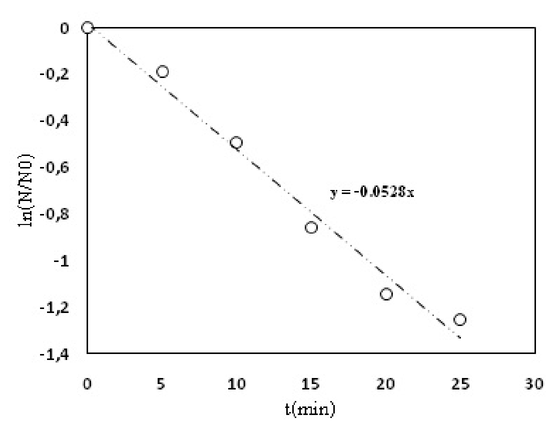

Figure 8: The effect of residual time on the absorption for 15gr adsorbent.

The effect of temperature on the disinfection process

The temperature of the system is another important parameter in the disinfection process. As seen from the figures and tables, high temperature kills more microorganisms such that the removal percent reaches 98.35 for 20 gr of adsorbent and mass flow rate of 10 in temperature 35 ^{o}C (figures 9-11).

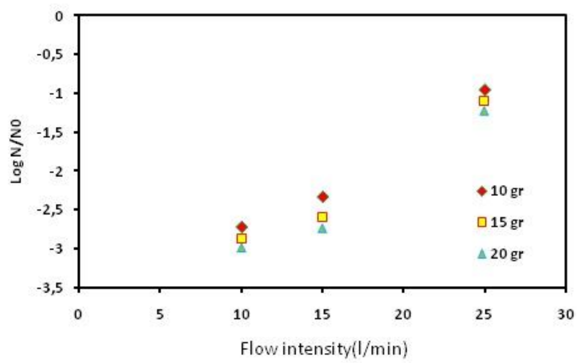

Figure 9: disinfection in T = 15 ^{0}C.

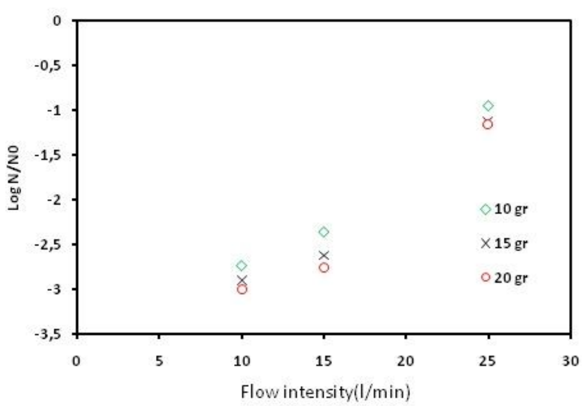

Figure 10: disinfection in T = 25 ^{0}C.

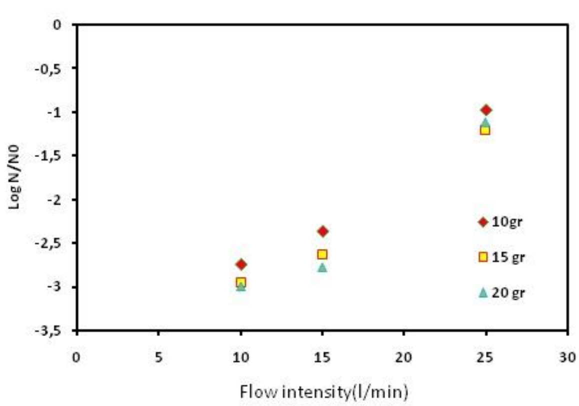

Figure 11: disinfection in T = 35 ^{0}C.

Synthetic model of disinfection with the modified magnetic mesoporous silica nanoparticles

In the present study, Chick-Watson model was used to develop a synthetic model. The microorganism removal is directly related to the disinfectant concentration and their contact time. That is, if the disinfectant concentration increases, the contact time should also increase. Increased contact time can cause a high inactivation of pathogens.

The disinfectant impact is expressed as Ct. C is the concentration of the disinfectant and t is the required time (in minutes) for the inactivation of microorganisms under the certain conditions (PH and temperature). Chick-Watson law shows the relationship between the disinfectant concentration and contact time (Cnt=K). K shows microorganisms which are in contact with the disinfectant under the certain conditions. n is the dilution coefficient. As seen from the below diagram, K is 0.0682 for Chick-Watson model (figure 12).

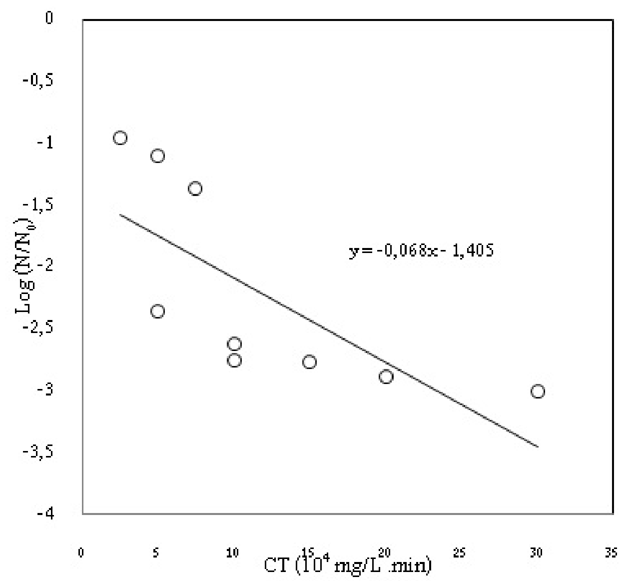

Figure 12: CT values of Chick-Watson model in water disinfection on the flow scale.

Conclusions

In this study, the disinfection of the drinking water with the modified magnetic mesoporous silica nanoparticles was investigated. First, raw water disinfection was conducted after the preparation of nanoparticles. Then, the pure water was contaminated artificially and the performance of these nanoparticles in the disinfection was investigated. Also, parameters affecting the microbial contamination were experimentally and artificially set and their effects on this process were examined. Parameters such as pH, temperature, time, water mass flow rate and tha adsorbent amount were tuned separately and the effect of each parameter with and without other parameters was investigated. The obtained curves are presented in results section.

The experiments were done by continuous phase method and disinfection index was based on the measuring factor MPN. In Flow method, a certain amount of the modified magnetic mesoporous silica nanoparticles was transferred into a column with a certain volume and contaminated water passed through it. The flow intensity was different for each measurement.

Water MPN was measured before and after passing the contaminated water. The optimal level of disinfection process was to achieve the biological standards for drinking water quality. Here, the output MPN was assumed to be 0.

The efficiency of the disinfection process was calculated using Chick-Watson law. For each method, Log (N/N0) values v.s. CT values were plotted. The obtained results show that the best PH in the disinfection process is 8. As the temperature increased, the system performance improved such that maximum absorption was in in T=35C. the absorption level increased over 99.82% with an increase in the adsorbent amount.

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