Nanoparticle Mediated Treatment of Dairy Wastewater

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Abstract. Nanotechnology is one of the emerging areas of scientific interest with numerous applications. In this research, surface modified silicon dioxide nanoparticules have been developed from low molecular weight chitosan by dip-coating technique for the batch treatment of dairy wastewater. The processing parameters of wastewater pH, mixing duration, agitation speed and quantity of nanoparticles are varied, and the treatment efficiency was established by measuring the total dissolved solids (TDS), turbidity, chemical oxygen demand (COD), total suspended solids (TSS), and dissolved oxygen (DO). Dynamic light scattering (DLS), scanning electron microscopy (SEM), energy dispersive X-Ray analysis (EDX), and fourier transform infrared spectrocopy (FTIR) are employed as characterization techniques. The DLS analysis showed the average diameter of the nanoparticles as 320 nm and the EDX analysis confirmed the elemental composition of the silicon dioxide nanoparticles. The functional groups are identified by FTIR. The optimum values for the best treatment conditions are established as pH 3.0, 60 minutes contact time, 100 rpm agitation speed and a nanoparticle dosage of 0.6 g. The batch expérimental study démontrâtes that the surface modified silicon dioxide nanoparticles could efficiently remove the polluants from the dairy wastewater in an environmentally friendly and cost effective method.

1 Introduction

Nanoengineered research and development of novel nanomaterials and methodologies have created a groundbreaking revolution in science and technology. The study and application of nanomaterials are considered as a promising area of research in food packaging, pharmaceutical, biomedical, advanced water treatment, renewable energy, and enhanced resource recovery applications [1–3]. The attractive properties of nanoparticles are suitable for the removal of toxic pollutants from wastewater owing to their outstanding physicochemical properties, strong oxidation capacity, enhanced thermal and chemical stability, and eco-friendly nature. Population expansion, climate change, prolonged droughts, and more strenuous regulations have resulted in severe environmental problem all over the world. The disposal of wastewater into open environment creates health and environmental problems [3-6]. The shortage of fresh water accompanied by the escalating

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pollution makes it unfit for drinking and other external uses [7]. Established wastewater treatment techniques normally consume more energy during the treatment processes and require high treatment cost leading to multiple health issues. Hence, it is highly recommended to develop a cost effective and ecofriendly method to treat wastewater, which is essential for a clean environment. Composite materials and membrane technology are gaining popularity due to their interesting pollutant removal efficiency [8]. Nanoengineered materials are trustworthy owing to their excellent specific surface area, smaller particle size, and outstanding surface functionality. Researchers are currently exploring novel techniques and emerging thoughts to enhance the effectiveness of water purification. The removal of organics, heavy metals, suspended solids, dissolved solids, and bacteria are carried out using different types of nanoparticles [9–13]. However, many of the treatment techniques remain ineffective for water reuse due to the presence of various contaminants [14]. Dairy industry is one of the leading process industries in Oman and consumes a huge volume of fresh water for different operational activities and discharges a considerable amount of toxic wastewater into the waterbodies leading to severe environment pollution. Therefore, it is essential to find a feasible solution to address this issue with the support of novel treatment techniques. Nanoparticle mediated treatment processes are a promising area of research for wastewater treatment applications due to their outstanding performance. Silicon dioxide nanoparticles are employed in various fields such as materials, medicine, engineering, pharmaceuticals, and wastewater treatment. Surface modified nanoparticles are one of the promising techniques to enhance the efficiency of pollutant removal. However, no major studies have been conducted by researchers to enhance the treatment of dairy effluents using polymeric nano particles. Therefore, the main objective of this research is to utilize polymer coated silicon dioxide nanoparticles for dairy wastewater treatment applications.

2 Materials and Methods

The precursor materials used for the synthesis of silicon dioxide nanoparticles are tetraethoxysilane, ethanol, and ammonium hydroxide. The biopolymer, chitosan, was used for the surface modification of silicon dioxide nanoparticles. Acetic acid was procured from Sigma Aldrich, Oman. All other chemicals used in the experiment are of high purity. Dairy wastewater was collected from a local milk processing unit in Oman. Stober's protocol was employed for the synthesis of silicon dioxide nanoparticles [15]. Silicon dioxide is prepared by the reacting the required composition of the precursor materials (tetraethoxysilane, ethanol, and ammonium hydroxide) at room temperature at a stirring speed of 150 rpm for 10 hours. The reaction mixture was separated by centrifugation at a speed of 5000 rpm followed by washing and drying to form fine powder. The resulting nanoparticles are surface modified using chitosan by dip coating technique to deposit the polymer. The surface modifies nanoparticles are centrifuged at 4000 rpm followed by repeated washing with deionized water and the resulting particles are used in the batch treatment of dairy wastewater.

The surface structural characterizations of the particles are carried out using a Field emission Scanning electron microscope (SEM JEOL JSM-7600F). The average diameter of particles before and after surface modification was determined using Dynamic light scattering (Mini Flex 600 DLS) and Fourier transform infrared spectroscopy (FTIR-FrontierTM is Perkin Elmer's) was employed for the identification of functional groups. The batch treatment of dairy wastewater was performed by amalgamating 250 ml of raw dairy wastewater and 5 ml of surface-modified particles in suspension form at room temperature. The efficiency of treatment process was studied by altering the processing conditions of wastewater pH, mixing duration, agitation speed and amount of surface

modified nanoparticles. The effectiveness of the treatment is calculated using the equation (i)

$$\% \text{ Reduction in parameter} = \frac{[A - B]}{A} x100 \quad \text{(i)}$$

where A and B are the initial and the final values in mg/l. Table 1 shows the dairy wastewater characteristics before treatment.

Table 1. Characteristics of dairy wastewater before treatment.

Parameter	Average value
Turbidity, NTU	324
TSS, mg/L	306
COD, mg/L	920
DO, mg/L	10
TDS, mg/L	190

2.1 Batch treatment of dairy wastewater

2.1.1 Effect of wastewater pH

The batch treatment of dairy wastewater was performed at room temperature (25 ± 2 °C) by mixing required amount of surface modified nanoparticles with 250 mL of dairy wastewater and kept under continuous stirring. The influence of solution pH on percentage removal of pollutants are studied in the pH range of 2.0 to 12.0 and the optimum parameter reductions are estimated by measuring the TDS, DO, TSS, Turbidity and COD.

2.1.2 Effect of stirring duration

Stirring duration plays a key role in lowering the pollutants from dairy wastewater. The influence of stirring duration on parameter reductions is reviewed by altering the stirring duration from 25 minutes to 150 minutes.

2.1.3 Effect of agitation speed

The influence of agitation speed was studied by varying the speed of agitation from 25 RPM to 150 RPM at optimized pH and stirring time. The effectiveness of the treatment efficiency was assessed by monitoring the COD, TSS, TDS, DO and turbidity of the raw and treated water.

2.1.4 Effect of dosage of nanoparticles

The influence of difference in weight dosage was examined by varying the dosage of quantity of coated nanoparticles from 0.1 g to 0.8 g and the reductions in parameters of TSS, COD, TDS, turbidity, and DO and were determined.

3 Results and discussions

The silicon dioxide nanoparticles are successfully synthesized, and the resulting particles were analyzed for SEM, EDX, DLS, FTIR and FTIR. Figure 1 shows the SEM micrograph of silicon dioxide nanoparticles at a magnification of 30,000×. The particles look intact, well dispersed and spherical in shape, which demonstrates the success of nanoparticle synthesis. The EDX spectra of the nanoparticles with elemental composition are indicated in Figure 2. The particle size analysis using DLS shows a single peak in Figure 3 confirms the particles are in uniform size and the mean diameter of the particle is around 330 nm.

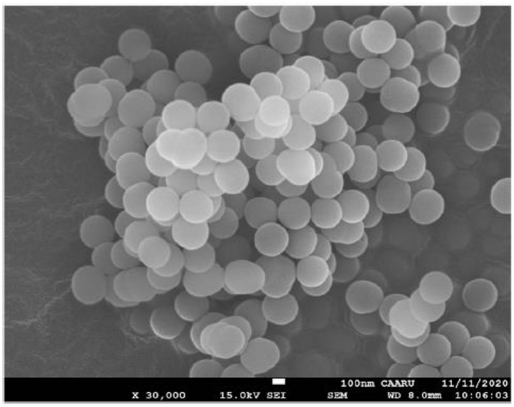

Fig. 1. SEM micrograph of silicon dioxide nanoparticles.

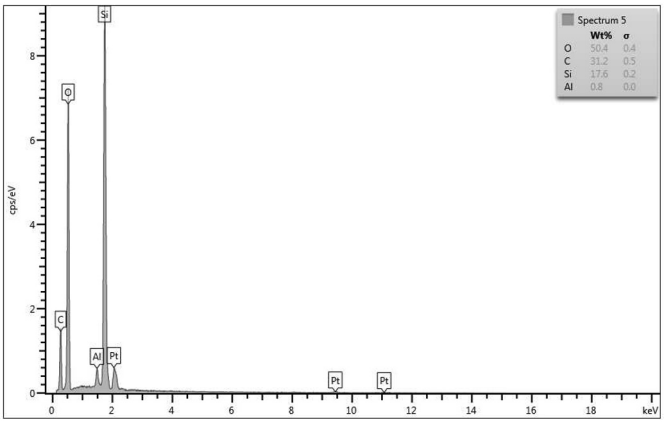

Fig. 2. EDX spectra of silicon dioxide nanoparticles.

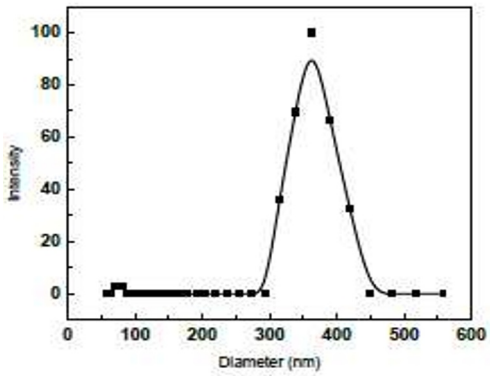

Fig. 3. Particle size analysis of silicon dioxide nanoparticles.

The surface functional groups of the coated nanoparticles are determined using FTIR as shown in Figure 4. The XRD spectra of the silica nanoparticles are shown in Figure 5. The morphological features of the surface modified silicon dioxide nanoparticles are shown in Figure 6. It is observed that the particles retained their original spherical shape with size slightly higher than silicon dioxide nanoparticles. The increased particle size is due to the enhanced deposition efficiency of chitosan on the surface of the particles, which shows the success of the uniform coating process. SEM image of coated particles in Figure 6 indicates that the particles are uniformly coated with chitosan and the surface becomes thick and shows scattered distribution.

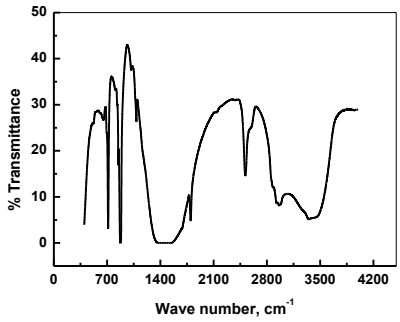

Fig. 4. FTIR spectra of silicon dioxide nanoparticles.

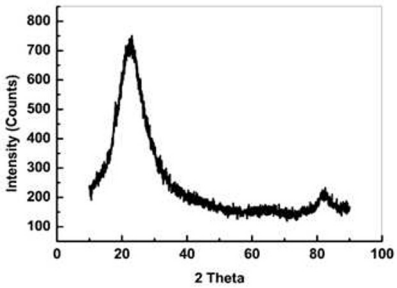

Fig. 5. XRD analysis of silicon dioxide nanoparticles.

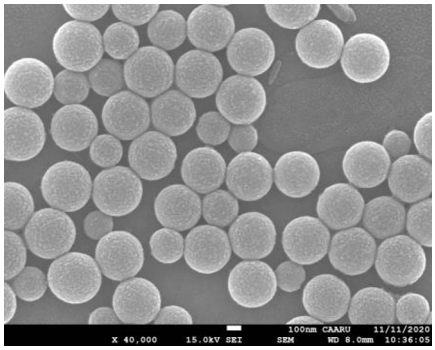

Fig. 6. SEM image of surface modified nanoparticles.

3.1 Treatment of dairy wastewater using surface modifies particles.

The coated nanoparticles are employed in the treatment of dairy wastewater by varying the pH from acidic to alkaline range (2.0 to 12.0), stirring duration (25 -150 minutes), agitation speed (25 rpm to 150 rpm) and the quantity of nanoparticles (0.1 g to 0.8 g). The effect of wastewater pH on the reduction of pollutants is normally related to the ionization condition of the surface modified nanoparticles and the nature of contaminants present in the wastewater. The best reduction in parameters is observed at pH 6.0. The study shows that COD, TDS, TSS, DO and turbidity increased with an increase in wastewater pH from 2.0 to 6.0, and above which there was a dip in the removal efficiency. The reason for increased efficiency is due to the enhanced surface charge of the particles with 2.0 pH to 6.0 pH and maximum surface charge appeared at pH 6.0 and this pH was considered as the optimum pH. Figure 7 indicates the influence of change in pH with pollutant removal.

The agitation duration is one of the significant factors determining the efficiency of wastewater treatment. The change in stirring duration on the parameter reductions is shown in Figure 8. The percentage reduction in parameters was favorable at the beginning (from 25 minutes to 75 minutes) and then showed a decreasing trend. The best COD reduction was obtained as 87% at 75 minutes of mixing duration. The extended mixing duration has resulted in lowering the removal efficiency and the optimal stirring duration was achieved at 75 minutes.

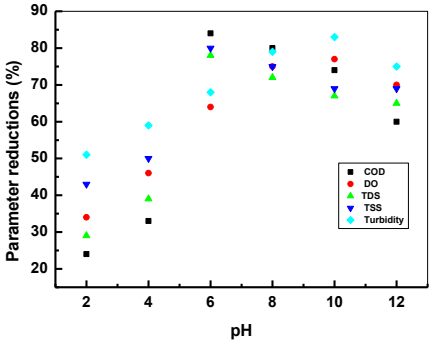

Fig. 7. Effect of pH on parameter reductions.

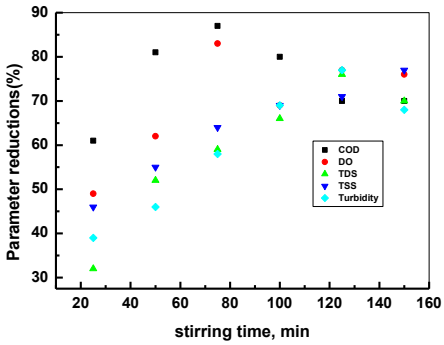

Fig. 8. Effect of stirring time on parameter reductions.

The influence of agitation speed with parameter reductions is obtained by altering the stirring speed from 25 to 250 rpm by keeping the optimal mixing duration of 75 minutes and wastewater pH 6.0. The influence of the agitation speed on pollutant removal is shown in Figure 9. The optimal agitation speed was observed at 100 rpm with a COD reduction efficiency of 83% as shown in Figure 9. The higher agitation speed results in over excitation of the particles, which will lead to the detachment of pollutants from to the particle surface and transfer to the bulk solution leading to decreased parameter reductions.

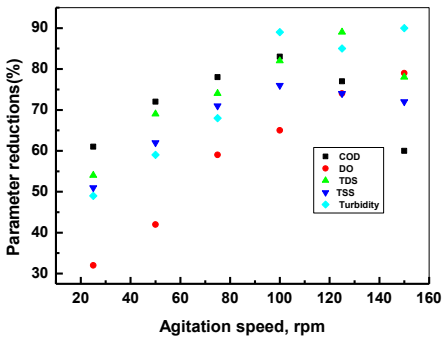

Fig. 9. Effect of agitation speed on parameter réductions.

The dosage of coated nanoparticles is a crucial factor contributing to the pollutant removal efficiency in wastewater treatment. The quantity of nanoparticles varied from 0.1 g to 0.8 g and the parameter reductions are measured. The increase in particle dosage showed a rise in the percentage removal efficiency as indicated in Figure 10. The increased dosage of nanoparticles resulted in enhanced surface area available for the adsorption process and hence more efficiency.

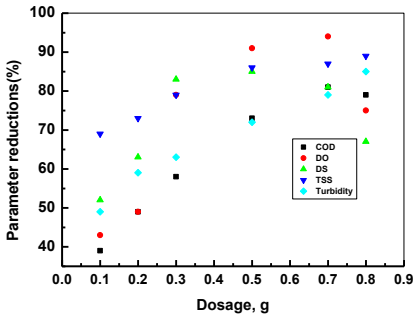

Fig. 10. Effect of nanoparticle dosage on parameter reductions.

4 Conclusions

Nanotechnology oriented treatment of dairy wastewater was carried out using surface modified nanoparticles. Silicon dioxide nanoparticles are successfully synthesized, and the resulting particles are surface modified using chitosan by dip coating technique. The various characterisation techniques using SEM, FTIR, DLS, XRD and EDX confirmed the successful synthesis of nanoparticles. The chitosan coated nanoparticles retained its spherical shape with scattered distribution. The batch experimental study of dairy wastewater using the surface modified nanoparticles displayed the optimum treatment parameters of pH 6.0, 75 minutes of stirring duration time, 0.7 g nanoparticle dosage and 100 rpm stirring speed. The SEM image of the nanoparticles after treatment showed excellent treatment efficiency surface functional characteristics and it was found that the chitosan coated silicon dioxide nanoparticles has a great potential in removing various pollutants from dairy wastewater in a cost effective and environmentally friendly way. This research supports the United Nations Sustainable Development Goals (SDG-6), which is clean water and sanitation.

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