An assessment on the effect of titanium dioxide & iron oxide nano-particles in industrial waste water decontamination

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Abstract. The aim of this paper is to identify a technique to detoxify the industrial waste water using metal oxide nanoparticles. Waste water from manufacturing or chemical processes in industries contributes to water pollution. Industrial waste water usually contains specific and readily identifiable chemical compounds. It destroys aquatic life and reduces its reproductive ability. Eventually it is hazardous to human life. Most major industries have treatment facilities for industrial effluents but this is not the case with small-scale industries, which cannot afford enormous investments in pollution control equipment. In this paper, an experimental study was conducted to study the effect of titanium dioxide and ferric oxide nanoparticles in detoxification of industrial waste water. Here the adsorption property of these nanoparticles was used for the detoxification of industrial waste water. The nanomaterials were synthesized using high energy ball milling machine and the characterization was done through scanning electron microscopy. After the preparation, these Nano sized titanium dioxide and ferric oxide powder were introduced to the pretested waste water. Due to the adsorption property of these nanomaterials, it is observed that the contaminants like sulphate, cadmium, lead and chlorides are adsorbed to some extent.

1. Introduction
Water pollution has been a major problem across the globe. The availability of safe drinking water has also been a prior concern across the globe. The water resources are depleted due to some reasons like, growth in population, extended droughts and pollutants from many industrial wastes. About 5 million people die each year from water related diseases and about 2.3 billion more suffer from diseases related to the drinking of contaminated water [7]. So the need for appropriate and cost effective wastewater treatment processes become essential for environmental conservation. The general wastewater treatment consists of two main processes: the first stage, where large objects such as sticks, stones and rags are removed, and the second stage is the biological treatment process, where the wastewater is purified by removing most of the contaminants [2]. This study is concentrated on the second stage process with the use of Titanium dioxide nanoparticles and ferric oxide nanoparticles as the adsorbent for the decontamination process. Nanotechnology has been used for the purification of water in the recent years, as it is highly effective in the decontamination of pollutants found in wastewater [2]. The effectiveness of wastewater treatments using nanotechnology to other existing techniques is high due to the high surface to volume ratio of the nanoparticles and hence the ability to reach all targeted compounds in the water [4].
This study aims at the utilisation of metal oxide Nano materials for the decontamination of industrial waste water. These include titanium dioxide nanoparticles and ferric oxide nanoparticles. The metal oxide particles have the ability to trap heavy metals in water, such as zinc, cadmium, lead etc. The synthesis of these nanoparticles were carried out using high energy ball milling machine at a constant speed. Different samples were prepared by varying the time for synthesis at constant speed. Industrial waste water samples were collected and was used for conducting adsorption experiments. Finally, a comparison study between these prepared nanomaterial samples were conducted and identifies which Nano-sample have maximum adsorption rate.

2. Materials and characterisation

2.1. Characterisation of water sample
The collection of wastewater sample for the study was an important aspect. The wastewater sample was collected from Milma Diary Thrissur. The collected wastewater sample was stored in a temperature of 15°C with a dilution of concentrated sulphuric acid. Generally strong acids such as HNO₃ and H₂SO₄ are used as diluting agents to prevent further chemical actions. Herein, based on the availability we dilute the samples with H₂SO₄ and the initial PH values are maintained even before each experiments. Pretesting was conducted to identify the contaminants present in the sample before adsorption experiments. Pretesting include testing of Dissolved Oxygen, chloride, sulphate, acidity test, alkalinity test and oil & grease test. The amount of free oxygen present in a water sample is generally termed as dissolved oxygen. The alkalinity and acidity results interpret the pH value of the sample. The pre-testing results are shown in Table 1.

| Pre-tests Wastewater sample (Milma) |
|-------------------------------------|
| Dissolved Oxygen                    | 0.921 mg/l |
| Chloride                            | 27.179 mg/l |
| Dissolved Sulphate                  | 1985.922 mg/l |
| Alkalinity                          | 4567.5 mg/l |
| Acidity                             | 118.8 mg/l |
| Oil & Grease                        | 452 mg/l |

Furthermore, the heavy metal presence in the waste water sample was found out using atomic absorption spectrometer. The observations obtained from atomic absorption spectrometer are as shown in Table 2.

| Heavy Metal | Wastewater sample (Milma) |
|-------------|---------------------------|
| Zinc        | Nil                       |
| Cadmium     | Nil                       |
| Magnesium   | Nil                       |
Table 2 shows that there are no heavy metals in the collected waste water sample. In order to determine the efficiency of titanium dioxide and iron oxide nanoparticles towards heavy metal adsorption, heavy metals are added manually to the waste water sample. 1g/L of cadmium sulphate and 1g/L of lead nitrate is mixed with the waste water sample. This manually prepared waste water sample was inspected through Atomic Adsorption Spectrometer, and the results were as shown in Table 3.

| Heavy Metal | Concentration of heavy metals in wastewater sample |
|-------------|---------------------------------------------------|
| Cadmium     | 250 mg/L                                           |
| Lead        | 20 mg/L                                            |

Now the wastewater contains 250 mg/L of cadmium and 20 mg/L lead content as shown in table 3.

2.2 Characterization of Nanomaterials
Nanoparticles formed by metal or metal oxides are inorganic nanomaterials, which are used broadly to remove heavy metal ions in wastewater treatment [5]. Nano sized metal oxide provides high surface area and high adsorption rates. Also, metal oxides have low impact on environment and low solubility and no secondary pollution [3]. So for this study, titanium dioxide and ferric oxide were selected and the size was determined using Scanning Electron Microscope (Hitachi SU6600). Titanium dioxide particle are in the range 134nm and ferric oxide in the range of 117nm which is shown in the Figure 1 and Figure 2.

![SEM image of TiO₂ powder before milling](image-url)
Figure 2. SEM image of ferric oxide powder before milling

The synthesis of nanomaterials from micro sized particles were carried out using high energy ball milling machine. Different range of nano particles were obtained by varying time (100hrs, 90hrs and 80hrs) at constant speed during the synthesis process and the average size of the particles are shown in the Table 4.

| Nanomaterial                | Speed (rpm) | Time (hours.) | Size (nm) |
|-----------------------------|-------------|---------------|-----------|
| Titanium dioxide            | 250         | 80            | 84.225    |
|                             | 250         | 90            | 71.9      |
| Ferric oxide                | 250         | 100           | 58.3      |
|                             | 250         | 80            | 72.7      |
|                             | 250         | 90            | 63.73     |
|                             | 250         | 100           | 42.11     |

Figure 3. SEM image of 100 hour milled TiO₂ powder
The size of the nanoparticles was measured using a Scanning Electron Microscope (Hitachi SU6600). The SEM images of the titanium nanoparticles and ferric nanoparticles are shown in Figure 3 to Figure 8.

![Figure 4. SEM image of 90 hour milled TiO₂ powder](image1)

![Figure 5. SEM image of 80 hour milled TiO₂ powder](image2)

![Figure 6. SEM image of 100 hour milled Fe₂O₃ powder](image3)
3. Testing and evaluation

After pretesting, the water samples are kept at lower temperature to reduce further chemical reduction. The post testing was carried out by mixing the nano particles synthesized with waste water sample. The three different sized nano powders of each metal oxides were introduced into the test wastewater samples for adsorption. A total of 6 samples were prepared for post testing. Trial and error method was used for selecting adsorbent concentration. The nano adsorbent was mixed to the wastewater sample using a glass beaker and glass rod. Then the sample was shaken well for 15 minutes for the adsorption to take place. During adsorption the voids present in the nano powder attracts the contaminants. After adsorption, the water sample was taken for post testing. Post testing includes heavy metal testing, Dissolved oxygen test, Alkalinity test, Acidity test, Chloride test, Sulphate test and oil and grease test. Heavy metal testing is done using Atomic Adsorption Spectrometer. Winkler’s method with starch as indicator was the basic principle of Dissolved oxygen test. The method of analysis of oil and grease in a water sample involves extraction of emulsified oil and grease from water by an extracting solvent. Chloride test was conducted by means of titration of standard silver nitrate solution with chromate indicator. The common solvents used are hexane and trichloro-trifluoroethane. The level of Sulphate in waste water sample was measured by turbidity metric method. Acidity of waste water sample was calculated through titration with a strong base to a designated pH and similarly alkalinity was measured with a strong acid namely hydrochloric acid. Same procedure is carried out using the two metal oxide nano powders, namely titanium dioxide and ferric oxide.

Figure 7. SEM image of 90 hour milled Fe₂O₃ powder

Figure 8. SEM image of 80 hour milled Fe₂O₃ powder
4. Results and Discussion
The post testing experiments were carried out with the nano powder mixed waste water samples with retention time 15 minutes and the corresponding results are shown in Table 5.

### Table 5. Post testing results of waste water sample (100 hours milled adsorbents used)

| Name of Test  | Adsorbent Dosage in grams | TiO₂ Test Results in mg/L | Fe₂O₃ Test Results in mg/L |
|---------------|---------------------------|---------------------------|----------------------------|
| Dissolved Oxygen | 0.01                       | 0.748                     | 0.823                      |
|                | 0.03                       | 0.973                     | 1.048                      |
| Dissolved Sulphate | 0.01                       | 1219.57                   | 939.39                     |
|                | 0.03                       | 741.63                    | 807.55                     |
| Chloride       | 0.01                       | 22.731                    | 19.48                      |
|                | 0.03                       | 17.86                     | 16.56                      |
| Acidity        | 0.01                       | 40.05                     | 48.95                      |
|                | 0.03                       | 31.15                     | 40.05                      |
| Alkalinity     | 0.01                       | 3940.5                    | 4100.25                    |
|                | 0.03                       | 3780.75                   | 4047                       |
| Oil and Grease | 0.01                       | 244                       | 252                        |
|                | 0.03                       | 172                       | 196                        |

### Table 6. Post testing results of waste water sample (90 hours milled adsorbents used)

| Name of Test  | Adsorbent Dosage in grams | TiO₂ Test Results in mg/L | Fe₂O₃ Test Results in mg/L |
|---------------|---------------------------|---------------------------|----------------------------|
| Dissolved Oxygen | 0.01                       | 0.748                     | 0.823                      |
|                | 0.03                       | 0.823                     | 1.048                      |
| Dissolved Sulphate | 0.01                       | 1285.49                   | 988.89                     |
|                | 0.03                       | 774.59                    | 856.94                     |
| Chloride       | 0.01                       | 25.978                    | 24.35                      |
|                | 0.03                       | 21.107                    | 18.18                      |
| Acidity        | 0.01                       | 53.4                      | 80.1                       |
|                | 0.03                       | 44.5                      | 66.75                      |
| Alkalinity     | 0.01                       | 4153.5                    | 4473                       |
|                | 0.03                       | 3940.5                    | 4313.25                    |
| Oil and Grease | 0.01                       | 384                       | 392                        |
|                | 0.03                       | 256                       | 268                        |

### Table 7. Post testing results of waste water sample (80 hours milled adsorbents used)

| Name of Test  | Adsorbent Dosage in grams | TiO₂ Test Results in mg/L | Fe₂O₃ Test Results in mg/L |
|---------------|---------------------------|---------------------------|----------------------------|
| Dissolved Oxygen | 0.01                       | 0.823                     | 0.898                      |
|                | 0.03                       | 0.898                     | 0.973                      |
| Dissolved Sulphate | 0.01                       | 1351.41                   | 1087.72                    |
|                | 0.03                       | 889.95                    | 939.39                     |
| Chloride       | 0.01                       | 27.601                    | 25.65                      |
|                | 0.03                       | 22.731                    | 21.43                      |
| Acidity        | 0.01                       | 71.2                       | 93.45                      |
|                | 0.03                       | 57.85                      | 80.1                       |
Table 8. Post heavy metal test results of waste water

| Heavy Metal | Adsorbent Dosage in grams | TiO₂ Test Results in mg/L | Fe₂O₃ Test Results in mg/L |
|-------------|---------------------------|---------------------------|---------------------------|
| Cadmium     |                           |                           |                           |
| 0.025       | 150                       | 140                       |
| 0.05        | 240                       | 210                       |
| 0.1         | 370                       | 235                       |
| 0.15        | 500                       | 260                       |
| Lead        |                           |                           |                           |
| 0.025       | 16.7                      | 16                        |
| 0.05        | 14.3                      | 11.5                      |
| 0.1         | 12.5                      | 4.2                       |
| 0.15        | 14.6                      | 15                        |

Comparing Table 1 and Table 5, it was clearly seen that the level of dissolved oxygen, dissolved sulphate, chloride, acidity, alkalinity and oil & grease content in the waste water sample reduced to some extent. In case of dissolved oxygen, ferric oxide improves the amount of free oxygen in the water sample at 0.01g of 100 hour milled adsorbent addition. From Table 5, it was clearly seen that at 0.03 g of nano ferric oxide addition the acidity of the waste water sample decreased to 30.05 mg/L from 118.8 mg/L of the pre waste water sample while titanium dioxide nanoparticle addition reduced the value to 31.15 mg/L. Also it can be observed that the acidity of the waste water sample can be reduced by increasing the adsorbent dosage. From Table 5, 6 and 7, it is observed that the adsorption capacity reduced when the milling time decreased. While observing Table 8, the maximum adsorption of cadmium and lead take place at 0.05g and 0.1g of adsorbent addition respectively. Also it can be observed that, after a certain level of adsorbent addition, the adsorption process seized. The above results show that the nano pores can adsorb general pollutants like chlorides, sulphates and heavy metals from water.

5. Conclusion
Nanotechnology for water and wastewater treatment is gaining momentum globally. The unique properties of nanomaterials and their convergence with current treatment technologies present great opportunities in the area of water and wastewater treatment. In this study the adsorption with metal oxide nanoparticles was successful in decontamination. The preparation of nanoparticle depends on the speed of rotation and milling time. The particle size of 42.11 nm and 72.7 nm were obtained from 100 hours and 80 hour milling of ferric oxide. Similarly, titanium dioxide having 58.3 nm and 84.225 nm size were obtained under same condition. Correspondingly the particle size increases as the milling time reduces. It is clear that the heavy metals and other contaminants get trapped in the pores of nano materials. Also the rate of adsorption depends on the adsorbent used. Here ferric oxide nanoparticles have greater adsorption efficiency than titanium dioxide nanoparticles towards cadmium and lead, that is 44% and 79% respectively. In case of dissolved oxygen, ferric oxide improves the amount of free oxygen in the water sample at 0.3 g/L of 42.11 nm Fe2O3 adsorbent addition. Similarly, ferric oxide shows better result in chloride and dissolved oxygen tests. Whereas titanium dioxide shows better performance towards Acidity, alkalinity and oil & grease test compared to ferric oxide. Collectively we can say that ferric oxide nano materials shows better adsorption towards heavy metals whereas titanium dioxide has greater results in general water quality tests. While comparing the adsorption qualities of the two nano- adsorbents ferric oxide shows better effectiveness, and the reason behind this effectiveness is still not clear, even though it may due to the
presence of more active pores available in the ferric oxide than titanium. Further researches are needed to make a last note on that. So a combination of these two nano materials can be utilized as one of the method for industrial wastewater treatment. Further study can be conducted using different nanomaterials to study their adsorption rates and its feasibility in industrial installation. Until now most of the nano materials are costly compared to conventional methods thus the future focus should be on reducing the financial problems associated with nanotechnology. Regeneration and recovery addresses two important aspects, namely, the adsorbents may become reusable, and regeneration of adsorbents makes the adsorption process economically viable. Further researches are needed to evaluate such aspects.

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