An experimental study on the effect of manganese dioxide & ferric oxide nano-particles for sewage water decontamination

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Abstract. The vision of this paper is to investigate and introduce a technique to decontaminate, one of the most essential commodities of life that is, water. The requirement of water for an individual varies from a minimum of 8 liters per day for drinking and cooking to about 20-50 liter per day for other daily needs. Unfortunately, about half of a billion people face the problem of water scarcity throughout the year. The treatment of wastewater namely sewage water can reduce these concerns however, the traditional methods of treatment are not efficient enough to completely remove the emerging pollutants. In this paper an experimental study was conducted for the effect of nano-sized materials on the purification of sewage water. As a matter of fact, various nano-materials have been prepared and used for the removal of contaminants from water. Herein the mechanism of adsorption was taken in to consideration were manganese dioxide and ferric oxide nano-particles were utilized as an adsorbent for decontamination of sewage water. The nano-materials were synthesized by means of planetary ball mills and characterization was done through scanning electron microscope. Then the prepared nano-particles were introduced in to the pre-tested water samples for contaminant adsorption. It was observed that the nano-materials can adsorb contaminants like zinc, magnesium, cadmium, chlorides & sulphates to some extent. In addition to this, the treated water shows excellent water quality standards.

1. Introduction
In the modern scenario of scarcity of water resources, effective and viable treatment of wastewater is essential for growing economy. It is important to introduce and implement advanced wastewater treatment technologies with low capital requirements. The treatment of wastewater namely sewage water can reduce the current concerns to some extent. Among various treatments, recent advanced processes in nano-sized materials have been attracting the attention of scientists towards wastewater treatments [1]. This article investigates the utilization of metal oxide nano-materials for wastewater treatment processes. This includes the use of manganese dioxide and ferric oxide nano-particles as nano-adsorbents.

One of the major advantage of nano-sized particles are the amount of surface they exposed to trap contaminants [4]. A surface phenomenon of adsorption is takes place in this large surface area and consequently hold the pollutants. The metal oxide particles have the ability to trap heavy metals in water such as, zinc, mercury, lead etc. The heavy metal adsorption depends on the type of the parent...
metal [2]. The presence of heavy metals, dyes and microorganisms even in trace amounts, are very dangerous to human health, aquatic systems and the environment.

This paper will discuss the potential role of engineered nano-materials such as manganese dioxide and ferric oxide for the development of water purification systems. Sewage water samples were utilized to perform the adsorption experiments and a comparison is carried out between the two types of nano-particles. In addition to this, the preparation of nano-adsorbents play a vital role in decontamination that is the preparation improves the particle nature. Herein, planetary ball mills were utilized to synthesize the nano-particles. By varying the speed and time of milling different nano-range can be achieved.

2. Materials and characterisation

2.1. Characterisation of water sample

One of the main aspects regarding the waste water selection is the type of sewage water, namely grey water. It is a type of water obtained from kitchen outlets. Herein two grey water samples one from an outlet of canteen and another from kitchen of a modern house is collected. The collected samples were stored in a temperature of 15 degree Celsius with a dilution of concentrated sulphuric acid. Before that, collected water samples were tested for identifying the amount of contaminants present in the water. The initial testing is somewhat called characterization of sewage water and in environmental engineering there are two standard tests based on the oxidation of organic material, that is biological oxygen demand and chemical oxygen demand. The biological oxygen demand of a sample is the amount of oxygen required for the decomposition of organic matter present in the water sample. The chemical oxygen demand gives the measure of the oxygen required for chemical oxidation. The pre-testing results are shown in Table 1.

| Pre-Tests                  | Kitchen Outlet Water | Canteen Water |
|---------------------------|----------------------|---------------|
| Dissolved oxygen          | 0.92mg/l             | 1.288mg/l     |
| Chemical oxygen demand    | 128.4mg/l            | 102.72mg/l    |
| Biological oxygen demand  | 136.4mg/l            | 157.6mg/l     |
| Chloride                  | 4.99mg/l             | 7.99mg/l      |
| Sulphate                  | 1606.805mg/l         | 2678.105mg/l  |
| Alkalinity                | 1260mg/l             | 577.5mg/l     |
| Acidity                   | 79.2mg/l             | 52.8mg/l      |

In addition to this, the presence of heavy metals in water can be tested by means of an atomic absorption spectrometer. Generally the presence of heavy metals are arises due to chemical reaction between molecules of kitchen cleaning agents and decomposed sewage. The atomic absorption spectrometer observations are as shown in Table 2.
Table 2. Heavy metals in water samples

| Heavy Metal | Kitchen Outlet Water | Canteen Water |
|------------|----------------------|---------------|
| Zinc       | Nil                  | Nil           |
| Lead       | Nil                  | Nil           |
| Cadmium    | Nil                  | Nil           |
| Arsenic    | Nil                  | Nil           |
| Magnesium  | 32.14 mg/l           | Nil           |

2.2. Characterization of nanomaterials
There are various adsorbents such as bio adsorbents, metal oxide and non-mental oxide adsorvents. From this, metal oxide based nano-materials shows excellent adsorption capacity towards heavy metals in water [2]. Magnesium and ferric oxide materials show sublime capacity to hold contaminants in nano ranges. They were purchased in their oxide form and its grain size is determined through scanning electron microscope. Manganese oxide particles are initially in the range of 361.875 nm and similarly ferric oxide particles are 110.514 nm, their images are shown in Figure 1 and Figure 2.

Figure 1. SEM image of Manganese dioxide powder

Figure 2. SEM image of Ferric oxide powder.
The SEM results shows that the particle size were above 100 nm and thus it is to be reduced to below 100 nm. The nano-particles of MnO₂ and Fe₂O₃ were prepared using the process of high energy ball milling using the equipment RETSCH PM100. The samples were collected on completion of 80 hours, 90 hours and 100 hours of milling operation and each of the samples were analysed for particle and crystal size. Table 3 shows average particle size of each adsorbent.

| Speed (rpm) | Time (hours) | Size (nm) |
|-------------|--------------|-----------|
| 250         | 80           | 80.025    |
| 250         | 90           | 71.73     |
| 250         | 100          | 49.34     |
| 250         | 80           | 72.11     |
| 250         | 90           | 63.73     |
| 250         | 100          | 42.11     |

Characterization of nano-materials includes the identification of average particle size and its crystal size. A simple sampling is carried out to determine the average particle size, that is, while observing through SEM only certain particles were randomly selected and average of the same is taken as the particle size of that group or sample. The average size may differ when we choose different particles at different locations. Samples were analysed by HITACHI SU 6600 Scanning Electron Microscope at NIT Calicut. Three samples at different conditions were observed through SEM at 30k magnification. The results of SEM are as follows:

![SEM image of MnO₂ at 100 hours](image-url)
Figure 4. SEM image of MnO₂ at 90 hours

Figure 5. SEM image of MnO₂ at 80 hours

Figure 6. SEM image of Fe₂O₃ at 100 hours
Testing and evaluation are the two premier components of this work. The pre-tested water samples were preserved in a low temperature atmosphere, this will reduce the chance of further chemical reduction in the water samples. The post-testing was carried out with mixing of nano-particles. The two different sized nano-adsorbents were introduced into the testing samples for adsorption. The amount of adsorbent used was selected based on the total amount of contaminants present in the samples. It is necessary to take a correction factor to avoid under and over adsorption of pollutants. Dilution and stirring of nanoparticles with wastewater was carried out by means of glass beakers and glass rods. After that the samples were undisturbed for adsorption to take place. During that period the available voids or adsorption sites were attracting the contaminants present in the sample. After adsorption the water samples were extracted for post-testing. Separation of nano-particles depends on the nature of the particle and the medium. The usual methods of separation include filtration, centrifugation and magnetic separation. Herein centrifugation followed by filtration was carried out. The same procedure is carried out with two metal oxide nano-powders.
4. Results and Discussion
The post testing experiments were carried out with the nano powder mixed waste water samples with a retention time of 15 minutes and the corresponding results are as follows;

**Table 4.** Post testing results of kitchen outlet grey water (nano-particle size: MnO₂ - 49.34 nm & Fe₂O₃ - 42.11 nm)

| Name of Test    | Adsorbent Dosage in grams | MnO₂ Test Results in mg/L | Fe₂O₃ Test Results in mg/L |
|-----------------|---------------------------|---------------------------|---------------------------|
| Dissolved Oxygen| 0.01                      | 1.578                     | 1.478                     |
|                 | 0.03                      | 3.5768                    | 2.9456                    |
| Dissolved Sulphate | 0.01                   | 834.03                    | 1483.2                    |
|                 | 0.03                      | 412.01                    | 659.22                    |
| Chloride        | 0.01                      | 6.16                      | 7.71                      |
|                 | 0.03                      | 1.54                      | 3.08                      |
| Acidity         | 0.01                      | 43.25                     | 51.9                      |
|                 | 0.03                      | 17.3                      | 25.95                     |
| Alkalinity      | 0.01                      | 468                       | 520                       |
|                 | 0.03                      | 312                       | 416                       |
| Oil and Grease  | 0.01                      | 68                        | 92.4                      |
|                 | 0.03                      | 28                        | 36                        |
| COD             | 0.01                      | 50.8                      | 76.32                     |
|                 | 0.03                      | 8.48                      | 25.44                     |
| BOD             | 0.01                      | 19.04                     | 19.59                     |
|                 | 0.03                      | 7.035                     | 7.59                      |

**Table 5.** Post testing results of kitchen outlet grey water (nano-particle size: MnO₂ - 71.73 nm & Fe₂O₃ - 63.73 nm)

| 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 6. Post testing results of kitchen outlet grey water (nano-particle size: MnO₂ - 80.025 nm & Fe₂O₃ - 72.7 nm)

| Name of Test      | Adsorbent Dosage in grams | MnO₂ Test Results in mg/L | Fe₂O₃ Test Results in mg/L |
|-------------------|---------------------------|---------------------------|----------------------------|
| Dissolved Oxygen  | 0.01                      | 1.578                     | 3.3664                     |
| Oxygen            | 0.03                      | 3.3664                    | 3.3664                     |
| Dissolved         | 0.01                      | 1318.45                   | 1499.74                    |
| Sulphate          | 0.03                      | 856.99                    | 1104.20                    |
| Chloride          | 0.01                      | 7.71                      | 7.71                       |
| Acidity           | 0.03                      | 47.575                    | 51.9                       |
| Alkalinity        | 0.03                      | 520                       | 520                        |
| Oil and Grease    | 0.03                      | 64.4                      | 68                         |
| COD               | 0.03                      | 59.36                     | 101.76                     |
| BOD               | 0.03                      | 7.035                     | 7.59                       |

Table 7. Post testing results of canteen grey water (nano-particle size: MnO₂ - 49.34 nm & Fe₂O₃ - 42.11 nm)

| Name of Test      | Adsorbent Dosage in g/L | MnO₂ Test Results in mg/L | Fe₂O₃ Test Results in mg/L |
|-------------------|--------------------------|---------------------------|----------------------------|
| Oxygen            | 0.01                     | 1.052                     | 0.9468                     |
| Dissolved         | 0.03                     | 2.314                     | 2.104                      |
| Sulphate          | 0.03                     | 329.61                    | 494.42                     |
| Chloride          | 0.03                     | 3.08                      | 4.62                       |
| Acidity           | 0.03                     | 56.225                    | 73.525                     |
| Alkalinity        | 0.03                     | 1092                      | 1196                       |
| Oil and Grease    | 0.03                     | 100                       | 148                        |
| COD               | 0.03                     | 67.84                     | 93.28                      |
| BOD               | 0.03                     | 20.76                     | 21.75                      |
Table 8. Post testing results of canteen grey water (nano-particle size: \( \text{MnO}_2 \) - 71.73 nm & \( \text{Fe}_2\text{O}_3 \) - 63.73 nm)

| Name of Test  | Adsorbent Dosage in g/L | \( \text{MnO}_2 \) Test Results in mg/L | \( \text{Fe}_2\text{O}_3 \) Test Results in mg/L |
|---------------|-------------------------|----------------------------------------|---------------------------------|
| Dissolved Oxygen | 0.01                    | 1.052                                  | 0.9468                          |
| Dissolved Sulphate | 0.03                    | 2.314                                  | 2.104                           |
| Chloride | 0.01                    | 3.08                                   | 4.62                            |
| Chloride | 0.03                    | 3.08                                   | 3.08                            |
| Acidity | 0.01                    | 64.875                                 | 73.525                          |
| Acidity | 0.03                    | 38.925                                 | 51.9                            |
| Alkalinity | 0.01                    | 1040                                   | 1196                            |
| Alkalinity | 0.03                    | 728                                    | 936                             |
| Oil and Grease | 0.01                    | 124                                    | 160                             |
| COD | 0.01                    | 76.32                                  | 118.72                          |
| COD | 0.03                    | 25.44                                  | 42.4                            |
| BOD | 0.01                    | 20.76                                  | 21.75                           |
| BOD | 0.03                    | 20.76                                  | 21.75                           |

Table 9. Post testing results of canteen grey water (nano-particle size: \( \text{MnO}_2 \) - 80.025 nm & \( \text{Fe}_2\text{O}_3 \) - 72.7 nm)

| Name of Test  | Adsorbent Dosage in g/L | \( \text{MnO}_2 \) Test Results in mg/L | \( \text{Fe}_2\text{O}_3 \) Test Results in mg/L |
|---------------|-------------------------|----------------------------------------|---------------------------------|
| Oxygen | 0.01                    | 1.052                                  | 0.9468                          |
| Oxygen | 0.03                    | 2.314                                  | 2.104                           |
| Dissolved Sulphate | 0.01                    | 1318.45                               | 1318.45                         |
| Dissolved Sulphate | 0.03                    | 1054.76                               | 1318.45                         |
| Chloride | 0.01                    | 4.62                                   | 4.62                            |
| Chloride | 0.03                    | 4.62                                   | 4.62                            |
| Acidity | 0.01                    | 73.525                                 | 73.525                          |
| Acidity | 0.03                    | 51.9                                   | 73.525                          |
| Alkalinity | 0.01                    | 1144                                   | 1196                            |
| Alkalinity | 0.03                    | 832                                    | 1144                            |
| Oil and Grease | 0.01                    | 148                                    | 196                             |
| Oil and Grease | 0.03                    | 124                                    | 160                             |
| COD | 0.01                    | 76.32                                  | 118.72                          |
| COD | 0.03                    | 50.88                                  | 42.4                            |
| BOD | 0.01                    | 33.42                                  | 48.73                           |
| BOD | 0.03                    | 20.76                                  | 21.75                           |
Table 10. Post heavy metal test results of kitchen outlet water

| Adsorbent Dosage (mg/l) | Magnesium Concentration (mg/l) | Adsorption percentage (%) |
|------------------------|-------------------------------|---------------------------|
| 0.025 Mno₂             | 18.80                         | 41.50                     |
| 0.05 Mno₂              | 21.13                         | 34.25                     |
| 0.10 Mno₂              | 25.09                         | 21.93                     |
| 0.15 Mno₂              | 29.05                         | 9.61                      |
| 0.025 Fe₂O₃            | 28.20                         | 12.25                     |
| 0.05 Fe₂O₃             | 10.98                         | 65.83                     |
| 0.10 Fe₂O₃             | 14.12                         | 56.06                     |
| 0.15 Fe₂O₃             | 15.84                         | 50.71                     |

While comparing the tables it is clear that the rate of adsorption depends on the size of nano-particles, when the size of nano-particles reduces, consequently the rate of adsorption increases due to large adsorption sites. In case of dissolved oxygen test 0.03mg/l dosage improves the values than 0.01mg/l concentration in all cases. In addition to this, after treating with nano-adsorbents a maximum value of about 3.5768mg/l and 2.314mg/l dissolved oxygen was found out in kitchen outlet and canteen water respectively at a concentration of 0.03mg/l MnO₂.

All tests except the test of dissolved oxygen shows reduction in initial concentration. More or less, again higher concentration of manganese di-oxide stands with better results than ferric oxide particles. In table 6 & 9 of post testing with 80 hour milled nano particles, adsorption rate is lesser than the other and most values remains unchanged from a 90 hour milled particle test.

In table 10 of magnesium metal test, adsorption rate is not uniform with the concentration of adsorbents. In case of manganese nano particles lesser dosage has the capacity to adsorb magnesium at a maximum rate, whereas ferric oxide shows changing adsorption characteristics throughout. It is interesting to see the increase in chloride content even after adsorption, and it may be due to the internal chemical reactions happened during the testing, while exposing to the environmental conditions.

In table 1, BOD value is more than COD for both kitchen outlet water and canteen water, which is not the general trend and it can happen rarely. In other tables too, the trend is not uniform and which may arises due to the effect of conditions and time we exposed to the samples during experiments.

5. Conclusion

There is no debate on efficiency of utilizing nano-materials in wastewater treatment; however this technology has some serious upsides that need to be implemented in detail. Here the adsorption with metal oxide nano-particles was quiet successful in decontamination. The results elucidate that the sewage water pollutants will trapped when nano pores are available. Firstly the milling time will considerably enhance the surface area by reducing particle size, here also 100 hour milled samples shows a nano range of about 40 – 70 nm. In most of the cases adsorption improves when adsorbent dosage increases, noticeably 0.03mg/l dosage of manganese di-oxide shows better results. The magnesium metal adsorption of ferric oxide and manganese di-oxide is somewhat interesting that is, at a minimum dosage of 0.025mg/l of manganese di-oxide the adsorption was about 41.25 % and after that adsorption decreases with dosage, whereas ferric oxide shows maximum adsorption of about 65.83% at 0.05mg/l dosage. After adsorption with nano-powders the sewage water samples characteristics approaching towards drinking water specifications. Until now, most of the nano-materials have not been cost-competitive when compared with conventional materials thus future
applications will focus on efficient processes which will reduce the financing problem related to nano science. 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.

References
[1] Santhosh C, Venugopal V, Jacob G, Jeong S K, Andrews N G and Bhatnagar A 2016 Role of nanomaterials in water treatment applications: a review Chemical Engineering Journal 306 1116-1137
[2] Singh N B, Nagpal G, Agrawal S and Rachna 2018 Water purification by using adsorbents: a review Environmental Technology & Innovation 11 187-240
[3] Mines P D, Andersen H R, Yavuz C T, Hwang Y J and Mogens 2016 Hybridized reactive iron-containing nano-materials for water purification Thesis Denmark DTU environment
[4] Muzammil A R, Miandad M W, Gehany F and Barakat M A 2016 Remediation of wastewater using various nano-materials Arabian Journal of Chemistry 10.004
[5] Khan S T and Malik A 2019 Engineered nanomaterials for water decontamination and purification: From lab to products Journal of hazardous materials 363 295-308

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