Evaluation of nanostructures for wastewater in removing heavy elements and their effect on pea plant growth (Pisum sativum)

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Abstract:
The study was conducted to find out to what extent non-conventional water utilization in the agricultural field is possible, e.g., wastewater treated with nanomaterial alternatives. The research encompassed two laboratory experiments: The first one was to discover the efficiency of the nanomaterial used to remove heavy elements, such as (Cu, Mn, Zn), from raw wastewater and the laboratory concentrations were () mg × L⁻¹; and the second one was to test the effect of Nanotreated water on the percentage of pea seed germination in sterile plastic pots and three duplicates per parameter as a vital indicator. The experiment parameters included: (T1) tap water; (T2) raw wastewater; and (T3) Nano-treated wastewater using TiO₂. As for the third experiment, it was field-implemented by cultivating the plastic pots in the greenhouse of the Department of Life Sciences, University of Samarra, at the onset of January 2019 to see the effect of Nano-treatment, used on concentrations of the heavy element of zinc, on the vegetative parts of the local pea plant.

Introduction:
Water is the secret of life and one of the critical priorities is to preserve and maintain. Moreover, focusing on water resources is one of the necessary things to secure the requirements of a comfortable life as well as its possibility of usage for multiple purposes such as home, medical, and agricultural uses (1). The possibility of providing high-quality water has become a crucial matter, as water is one of the most endangered resources, and the use of ineffective methods has resulted in wasting more than 50% of the water in the local, industrial, and agricultural sectors.
Therefore, the objective of the present study is to evaluate unsafe wastewater resulting from domestic, industrial, and pharmaceutical uses, as it contains solid materials (organic and mineral) and high concentrations of heavy elements. Nonetheless, such water consists of 99.9% water and 0.1% suspended substances (2,3). One of the most important environmental pollutants is heavy elements, which include over 38 elements, some of which are necessary for biological activities, such as iron, while others are toxic, such as lead and selenium (4).

The problem of water contaminated with heavy elements encouraged some scientists to find different solutions and techniques such as the use of nanoparticles in treatment (5), which is one of the modern methods used to improve many of the water characteristics by its effect on a set of physical, chemical and biological characteristics. These particles help to treat contaminated wastewater by the adsorption process, which is an effective process and a safe and economical way altogether to remove metal ions from wastewater. However, a significant positive change in the characteristics of water was observed when using nanoparticles (6).

Titanium dioxide is one of the inexpensive, non-toxic nanomaterials that can be easily prepared and features high stability, excellent optical stimulation characteristics, and visual and electrical characteristics and has a series of environmental, medical, and biological applications, including water technology, drug transportation, paint, optical sensors, and solar cells. On this basis, it has been used on a wide scale and multiple applications (7).

Some studies have been conducted on the effect of nanomaterials in wastewater treatment. The zinc oxide was used (8) as a catalyst in treating the water of textile industries under UV rays; different concentrations have been used and the pH value has been changed to reach the highest rate of decomposition of the pigments. Furthermore, zinc oxide has proven highly effective in the decomposition of pigments formed in the textile industries, as the highest decomposition rate reached is (83%) at room temperature and within 205 minutes only. It has been proven that the textile
waste interacts effectively with the catalyst used and achieve good results in the decomposition of stuck histological particles.

Peas are a leguminous winter vegetable that is desirable in nutrition due to the high nutritional value of protein, as it is cultivated for their seeds that are consumed either green or dry, and then kept frozen or canned (9). Peas belong to the Leguminosae family, which contributes to maintaining soil fertility and enriching it with nitrogen, thanks to the root nodes that Rhizobium Leguminosarum bacteria form on the roots of pea plants through the coexistence of the plant and bacteria (10). The root system of peas is characterized by its ability to absorb large quantities of nutrients found in the soil. In fact, plants in the first stage of their life need certain amounts of elements, especially nitrogen (11). Due to the lack of rain in the winter and the abundance of wastewater, the desire to identify the effect of Nano–treatment in the percentage of germination and growth of peas has emerged to benefit from it for multiple purposes.

**Working methods:**

Two laboratory experiments were conducted, the first one is in the laboratories of the Department of Environmental Engineering, College of Engineering, Samarra University, in order to know the optimal concentration of titanium dioxide TiO$_2$ in removing heavy elements, such as copper, manganese, and zinc, from the raw wastewater selected in the study. However, the used concentrations of the nanomaterial (10 , 15 , 20 , 25 ) mg.L$^{-1}$, were based on what (12) mentioned. The water samples to be treated were placed in 1000 ml cylinders, then TiO$_2$ nanomaterial was added according to the above concentrations, manufactured by DuPont, gradually at pH 7.7 and 24 °C individually. Then, the water was mixed with the nanomaterial using the Jar Test device, manufactured by GAZAL.LTD company, for 150 minutes, after which the concentrations of the above mentioned heavy elements were measured by the Atomic Absorption Spectrophotometer (ASS), manufactured by PERKIN ELMER.USA. That is, to find out which concentration achieved the best percentage of removal of heavy elements, and the results showed
that the concentration of mg × L^{-1} achieved the best percentage in treating heavy elements (copper, manganese, and zinc) in raw wastewater. Based on the result the best concentration was 25 mg.L^{-1} used to study its effect on the seed germination characteristic.

Pic(1): Raw wastewater before treatment

Pic(2) :Wastewater treated with concentrations (10,15,20,25) mg.L^{-1}
Wastewater samples were taken from the primary treatment tanks from the main treatment center in Samarra city in 10–liter, plastic, graduated containers, and then the Nano–treatment was carried out with the addition of 25 mg.L⁻¹ of TiO₂ nanomaterial, and mixed well with a homemade, multi–speed mixer, used as needed. The treated solution was left for 150 minutes, and then the filter was transferred from the treated water to sterile glass bottles for the purpose of testing the ratios for removing heavy elements (Cu, Mn, Zn).

The second experiment was carried out in the laboratories of post–graduate studies, Department of Life Sciences, University of Samarra, which was undergoing an estimation of the percentage of germination of pea seeds as a result of the impact of the TiO₂ nanomaterial–treated wastewater compared to tap water and raw wastewater. However, the seeds were put after washing well with distilled water in sterile plastic pots with a diameter of 10 cm, in which are the filter paper, 10 seeds for each, and three duplicates so as to have 9 cultivated pots. The seeds were watered with water parameters used in the experiment to the extent of impregnation, then placed in the incubator at a temperature of 27 °C and after 7 days from the start of the experiment, the percentage of germinated seeds was recorded, according to (13).

\[
\text{Germination percentage} = \left( \frac{\text{number of germinated seeds}}{\text{total number of seeds}} \right) \times 100
\]
Pic (3): Seed with dishes before germination, three treatments

Pic (4): Seed with dishes after germination, three treatments

As for the field experiment, it was carried out in the greenhouse of the Department of Life Sciences, Samarra University, to know the effect of the various water parameters, which included (T1) tap water parameter, (T2) wastewater parameter, and (T3) Nano-treated wastewater in concentrations of the heavy element of zinc in the vegetative parts of the local pea plant.

Sterile, plastic, ready-made 12 kg pots were prepared, filled with sifted soil of 10 kg, and then 10 seeds were planted in each Pot⁻¹.
In the first week of January 2019, it was watered according to treatment parameters of the wastewater and control group with the same amount of water for each pot. After 15 days from seed germination, plants were reduced to 5 seeds per pot.

US–made titanium dioxide (TiO$_2$) was used with the size of 25 nanometers and at a concentration of 25 mg.L$^{-1}$, and after the harvest stage of cultivation, measurements were made of the vegetative parts of the pea plant to determine the concentration of heavy elements in such.

**Results and discussion**

The results of Figure (1) show the effect of water treatment with titanium nanomaterial's on the copper element. The results showed that there were significant differences between the parameters, as the Nano–treated parameter gave a significant decrease in the average of copper (0.3) mg.L$^{-1}$, compared to the average of copper in the untreated wastewater parameter of (1) mg.L$^{-1}$. Meanwhile, the tap water parameter recorded a concentration of (0.02) mg.L$^{-1}$. This decrease may be attributed to the effectiveness of TiO$_2$ in the wastewater parameter due to the high efficacy of sedimentation and adsorption of solid pollutants and complex organic compounds (14), and these results are consistent with (15) in study.

![Figure (1): Wastewater treated with concentrations (10, 15, 20, 25) mg.L$^{-1}$ in the Copper element compared to tap water and raw wastewater.](image)
The results of Figure (2) showed significant differences between treated and untreated parameters. The highest values of manganese in untreated wastewater recorded a value of (0.5) mg.L\(^{-1}\). While the treated wastewater recorded a significant decrease in the values of copper up to (0.06) mg.L\(^{-1}\), which was significantly similar to the control group parameter that recorded a concentration of (0.02) mg.L\(^{-1}\). This decrease in the percentage of removal of polluted elements may be attributed to nanoparticles using the coagulation and sintering processes as a result of adding the water, as the pollutants are agglomerated by sedimentation into small lumps of mass and then to larger particles. That is, the element of TiO\(_2\) nanomaterial is used as a main sinter\(^{(16)}\), and this study is consistent with what is said \(^{(17)}\) in study.

![Figure 2](image)

**Figure (2):** Wastewater treated with concentrations (10, 15, 20, 25) mg.L\(^{-1}\) in the Manganese element compared to tap water and raw wastewater.

The results of Figure (3) showed a significant difference between treated and untreated parameters. The highest values of zinc in untreated wastewater recorded a value of (3) mg.L\(^{-1}\), Whereas the treated wastewater recorded a significant
decrease in the values of copper up to (0.04) mg.L⁻¹, which was significantly similar to the control group parameter that recorded a concentration of (0.05) mg.L⁻¹. This decrease may be attributed to the percentage of removal of polluted elements due to the use of TiO₂ nanoparticles that helped to remove heavy metals from wastewater through adsorption by a noticeable decrease in pH(18) and these results are consistent with what said (19) in study.

Figure (2): Wastewater treated with concentrations (10, 15, 20, 25) mg.L⁻¹ in the Zinc element compared to tap water and raw wastewater.

Table (1) shows the effect of TiO₂ treated wastewater on germination percentage, treatment 3 significantly increased the men seed germination, It achieved a germination rate of 90% when compared to the treatment given 70% an increase (22.22%), the increase in average germination rate may be attributed to improvement of the physical and chemical wastewater properties as a result of adsorption of nanomaterial's from its aqueous solution (20) and these results are consistent with what said (21) in study.
Table (1): Wastewater treated with concentrations (10, 15, 20, 25) mg.L\(^{-1}\) in the percentage of seed germination laboratory compared with tap water and wastewater.

The results of Figure (5) showed significant differences between treated and untreated parameters in the vegetative parts of the plant. The highest values of zinc in untreated wastewater recorded a value of (69.5) mg.L\(^{-1}\), whereas the treated wastewater recorded a significant decrease in the values of copper up to (45.0) mg.L\(^{-1}\), which was significantly differed to the control group parameter that recorded a concentration of (64.2) mg.L\(^{-1}\). The decrease in the treatment of nanoparticles of the plant may be attributed to the efficiency and effectiveness of the nanoparticles through an adsorption mechanism that dissolves minerals and nutrients and facilitates their absorption and transfer. These results are consistent with what said (23) in study.
Figure (5): Wastewater treated with concentrations (10, 15, 20, and 25) mg.L⁻¹ in the vegetable parts of the Zinc element compared to tap water and raw wastewater.

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