STUDIES ON NITRATE REMOVAL FROM WASTEWATER USING NANO ZINC PEROXIDE AS ADSORBENT

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ABSTRACT
Nitrate pollution in underground water has become a constantly increasing environmental hazard. The usage of pesticides in agriculture leads to the intrusion of enormous quantities of nitrate ion into underground and surface water. Zinc peroxide is usually used in the rubber industry and for processing of plastic and functions as an oxidant and oxygen giver in compositions containing explosive constituents and pyrotechnical mixtures. Numerous techniques are available for the removal of nitrate from water samples. Several techniques for the elimination of nitrate from aqueous solutions have been explored but the adsorption process has been proven to be a very cost-effective technique for removal of nitrates. The objective of the present work is to prepare novel adsorbent for removal of nitrate from aqueous solution. Zinc Peroxide nano adsorbent was synthesized using two methods, novel oxidation–hydrolysis–precipitation and precipitation methods. These two techniques were chosen for its simplicity and ease of conduction. The adsorbent was characterized by X-ray diffractometer (XRD) and Scanning Electron Microscopy (SEM). Studies were conducted on different nitrate concentration samples. The effects of pH on the adsorption were studied to optimize the range. The effects of adsorbent dosage contact time and initial nitrate concentration on the adsorption process was also studied in the present work. The crystal size of the compound synthesized is calculated using the Scherrer method and found to be in the range of 60-80 nm. Experimental studies show that 75% nitrate was removed from a 14 ppm nitrate solution at a pH of 3 with a contact time of 4 hours. As the adsorbent dosage increased, adsorption also increased, and the optimal value is observed to be 40 g/L. The adsorption follows the Langmuir adsorption isotherm implying monolayer adsorption.

Keywords: Zinc peroxide Nanoadsorbent, Nitrate, Oxidation-hydrolysis-precipitation, Precipitation Method, Adsorption Isotherm, Adsorption Studies.

INTRODUCTION
Groundwater aids as the source of drinking water. In recent years, augmented industrial and agricultural activities have given the rise in the production of contaminated impurities such as inorganic, organic chemicals and metal ions, which have increased alarming concentration levels in the groundwaters. Inorganic anions are toxic and harmful to humans and animals at very low concentrations (ppb). Increasing nitrate levels in drinking water cause adverse health effects. Researchers have studied the removal of higher to a lower concentration of trivalent, hexavalent chromium, cadmium alone polyvinylpyrrolidone (PVP) functionalized zinc peroxide nanomaterial. The nanomaterial for total chromium was found to be 4.98 mg g-1 adsorption capacity of functionalized ZnO much higher than the other materials stated in the literature for chromium removal. Zinc peroxide is an important wide bandgap semiconductor material that has been extensively used. Adsorption and catalytic degradation of organic dyes were investigated using mixed oxides (ZFOs). In the present study zinc peroxide, nano adsorbent was synthesized using two methods, novel oxidation–hydrolysis–precipitation and precipitation methods removal of nitrate.

EXPERIMENTAL
Preparation of Zinc peroxide Using Method I
3 gms of zinc acetate dehydrate were added in 30 ml of distilled water and further, 15ml of 30% hydrogen peroxide was added. 30ml of PEG was later added to the mixture. The resulting mixture was
kept for 2 hours stirring. The solution obtained was pale yellow. Sodium hydroxide solution of pH 13 was added to create a basic medium till the 11.5 pH was obtained and the final mixture was a white color suspension. The white precipitate was centrifuged and the powder was washed three times with sodium hydroxide solution. Additional washes by distilled water were given till pH of 8.4 was obtained.

**Preparation of Zinc Peroxide Using Method II**

100 ml of zinc nitrate aqueous solution and 100 ml of sodium hydroxide solution were mixed and for two hours. The precipitate was separated and dispersed in 100 ml of H$_2$O$_2$ solution. The precipitate was later separated by centrifugation and dried at 75°C to obtain Zinc Peroxide nanopowder.

**RESULTS AND DISCUSSION**

**Characterization of the Zinc Peroxide Samples**

Zinc peroxide prepared using the method I was characterized using the X-Ray Diffraction method as shown in Fig.-1. The XRD pattern of the compound synthesized using the method I used zinc acetate reagent. The pattern matched with Standards data and was found to be pure ZnO$_2$ phase.

Zinc peroxide was prepared using method II, using Zn(NO$_3$)$_2$ as the reagent was characterized using X-Ray Diffraction. XRD pattern of the prepared compound is shown in Fig.-2 using method II and this pattern also in line with standard data.
Morphology of Zinc Peroxide Samples
The surface morphology of the nano zinc peroxide powder synthesized using method I and method II is shown in Fig.-3. SEM image shows polygonal morphology, this is due to the agglomeration of particles after synthesis.

Adsorption Studies of Nitrates
Numerous materials are explored as adsorbents for the removal of nitrates. Double layered hydroxides/hydrotalcite-type compounds and impregnated/modified-functionalized chitosan and its derivatives have shown a higher adsorption rate compared to other adsorbents. Surface modification of agricultural waste has also proved as an effective adsorbent for NO$_3^-$ removal and in some cases, these materials have shown a significant potential for nitrate removal.

The percentages of removal of nitrates are calculated as follows:

$$\% \text{ Adsorption} = \left\{ \left[ C_o - C_t \right] / C_o \right\} \times 100$$

Effect of pH
The effect of pH was studied over a range of 3 to 12. 1g of zinc peroxide powder was added to each sample solution. The solutions were kept for stirring at 150 rpm for 1 hour in a rotary shaker. The solutions were centrifuged in a microcentrifuge at 13200rpm to separate the nanopowder. The nitrate removal at different pH was shown in Fig.-4. pH plays a most significant role in the adsorption process for nitrate as it controls the charge of the adsorbent, the degree of ionization of the adsorbate in solution and facilitates the solid/liquid interface during the adsorption process. It was observed that adsorption decreases with an increase in pH. Hence, an acidic medium of pH 3 favors the adsorption of nitrate on zinc peroxide nanopowder.

$$\% \text{ Adsorption} = \left\{ \left[ C_o - C_t \right] / C_o \right\} \times 100$$

Fig.-4: Effect of pH on the Removal of Nitrate
Effect of Time
Experiments were carried out at different time intervals using the same amount of adsorbent dosage (40 g l\(^{-1}\)) and 25 mL volume of 25 mg l\(^{-1}\) concentration of nitrate solutions and results are shown in Fig.-5. It is observed that the removal of nitrate increases on increasing time till 240 minutes and remains constant thereafter. Also, the adsorption process has reached equilibrium at 240 minutes, hence the contact time is 4 hours.

**Fig.-5: Effect of Contact Time on Removal of Nitrate**

Effect of Initial Nitrate Concentration
Nitrate concentration was varied from 14–70 mg N/L and removal of nitrate was depicted in Fig.-6. Results have shown that nitrate removal decreases from 75 to 13% as the concentration of nitrate increases from 14 ppm to 70 ppm.

**Fig.-6: Effect of the Initial Concentration of Nitrate Removal**

Effect of Adsorbent Dosage
The effect of adsorbent doses was studied (40 g l\(^{-1}\)) with 25 mL of 25 mg l\(^{-1}\) concentration of nitrate at 240 minute period at pH 3. From Fig.-7, it is clear that there is no significant increase in adsorption with an increase in adsorbent dosage after 1 g for 25 mL of 25 mg l\(^{-1}\) nitrate solution.

**Fig.-7: Effect of Adsorbent Dosage of Nitrate Removal**
Adsorption Isotherm Studies

**Freundlich Isotherm**

Adsorption Equilibrium data were fitted to the Freundlich isotherm in Fig.-8 which indicates that the adsorption experimental data of nitrate on zinc peroxide does not fit with Freundlich equation assumptions, implying that the adsorption of nitrate on to the zinc peroxide does not take place on heterogeneous sites.

![Fig.-8: Freundlich Isotherm for Adsorption of Nitrates on Nano Zinc peroxide](image)

**Langmuir Isotherm**

The Adsorption equilibrium data were fitted to the Langmuir isotherm in Fig.-9. The adsorption follows the Langmuir isotherm proving that the adsorption occurring is monolayer adsorption which means that there is no stacking of adsorbed molecules.

![Fig.-9: Langmuir Isotherm for Adsorption of Nitrates on Nano Zinc peroxide](image)

**CONCLUSION**

In the present study, Pure phase zinc peroxide nanopowder was synthesized using both, oxidation-hydrolysis-precipitation and precipitation methods. From experimental studies, zinc peroxide produced from the oxidation-hydrolysis-precipitation method was more stable. Adsorption studies on the removal of nitrates using nano zinc peroxide. It was proved that percentage of nitrate removal decreases from 75% to 13% as the initial nitrate concentration increases from 14ppm to 70 ppm. There is no significant increase in adsorption with an increase in adsorbent dosage after 1g for 25 mL of 25 mg l$^{-1}$ nitrate solution. It is observed that the adsorption process has reached equilibrium at 240 minutes hence the contact time is 4 hours. An acidic medium of pH 3 favors the adsorption of nitrate on zinc peroxide nanopowder. Zinc peroxide has a good capacity to adsorb nitrates. Nano Zinc peroxide is divalent which can be used for adsorption of various ions like chromium, sulphur, chloride etc.

**REFERENCES**


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