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NITRATES IONS EFFICIENT REMOVAL FROM WATER USING THREE NANO ADSORBENTS

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Abstract: The increase of the input of nitrogen into environment as a result of human activities caused the increase of nitrates concentration in surface water. Consequently, the nitrates inputs have exceeded the assimilation and elimination capability of the biosphere. Intensive agricultural production, domestic and industrial wastes and atmospheric nitrogen pollution are some of the main sources of nitrate pollution of water. This study presents an efficient way of nitrate ions removal from water by using three adsorbents: Pd-Sn/ γ -Al₂O₃, NiTiO₃ and NiFe₂O₄. Also, we describe the preparation of Pd-Sn/ γ -Al₂O₃ by sol-gel method starting from Al(OC₃H₇)₃, PdCl₂ and SnCl₂. The obtained Pd-Sn/ γ -Al₂O₃ was structural and morphological characterized by scanning electron microscopy (TEM), X-ray diffraction (XRD) and BET analysis.

Keywords: nitrate ions pollution, adsorbant nanomaterials, water treatment

1. INTRODUCTION

Nitrate ions exist naturally in soil and water, but increased levels of nitrates are considered to be pollutant for groundwater and surface waters. In unpolluted areas, water has less than 1 mg/L of nitrates. Higher levels of nitrates typically correspond to compromised water [1-3]. Nitrate levels above the EPA Maximum Contaminant Level of 10mg/L N- NO₃ or 45 mg/L NO₃ may cause methemoglobinemia (also known as blue baby syndrome) in infants [4]. High levels of nitrate ions concentration in drinking water has the ability to impaired blood to carry oxygen throughout the body causing cancer, disruption of thyroid function, birth defects and other health risks. Only testing can determine nitrate in water, as nitrate has no taste, odor or color [5-7].

One of the sources of excess nitrates besides human and animal wastes or industry comes from agricultural activities. Nitrates are water soluble, easily carried by water and move freely through most soils. As regarding agriculture, nitrogen fertilizers (such as ammonium sulfate, ammonium chloride, ammonium nitrate, urea etc.) are applied on land surface to promote the growth of plants. During the rainfall or irrigation, ammonia (NH₄⁺) contained by fertilizer can leach into the ground below the root zone, reaching into the groundwater and rivers converting to nitrates (NO₃⁻) according to the following potential reactions (Fig. 1):



Nitrate ions concentrations from surface water coming from agriculture are primarily from groundwater connections and other subsurface flows. Another agriculture practice which consist

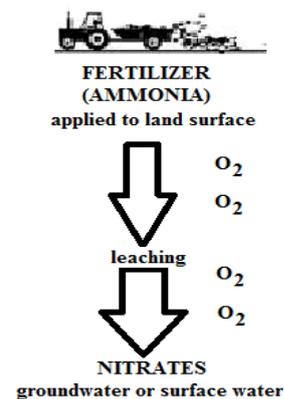


Fig. 1 - Schematic presentation of leaching ammonia from fertilizer to groundwater as nitrates

of the utilization as fertilizers the animal manure is also a dominant source of nitrate pollution of water. Conventional water treatment methods, such as sedimentation, filtration, chlorination or neutralization, do not efficiently remove nitrates from water. Nitrates from water can be removed by specialized water treatment technologies, such as ion exchange, biochemical denitrification, reverse osmosis and so one.

In this study we chose to study the removal of nitrates ions from water by adsorption on three different adsorbents.

2. MATERIALS AND METHODS

2.1. Adsorbent materials preparation

The Pd-Sn/ γ -Al₂O₃ material was obtained in two steps.

- ✓ Firstly γ -Al₂O₃ was prepared by sol-gel method in the presence of a template agent (lauric acid). The Al(OC₃H₇)₃: C₁₂H₂₄O₂ : C₄H₉OH molar ratio was 1: 0,15: 30. The aluminum precursor and water molar ratio was 1: 1,9. The reaction mixture was kept under reflux at 80°C for 100h, until a white precipitate was formed. The precursor was washed several times with alcohol, filtered, dried in air and calcined at 600°C for two hours.
- ✓ Secondly, the bimetallic material was prepared by sol-gel method using the precursor salts PdCl₂ and SnCl₂ in an ethylene glycol solution brought to pH 11 by addition of ammonia. The Pd-Sn/ γ -Al₂O₃ material contained 1 wt% noble metal (Pd) and 1 wt% Sn. The mixture was stirred for 12 h, under reflux and then ammonia and ethylene glycol were removed by washing several times with alcohol. After drying overnight at 90°C, the material was calcined at 200°C for 1h. The material finally obtained was analyzed by scanning electron microscopy (TEM), X-ray diffraction (XRD) and BET analysis.

The preparation and characterization of NiFe₂O₄ and NiTiO₃ was published elsewhere [8].

2.2. Nitrates analysis method

The analysis of nitrates from wastewater was determined using a standard method, no. SR ISO 7890/3-1998 applied for drinking water, surface water and wastewater. Adsorption experiments were carried out in Erlenmeyer flasks using a temperature controlled orbital shaker (stirring speed of 200 min⁻¹) for 36h. Twenty milligrams of the adsorbent were contacted with 50 mL of nitrate solution solutions (concentration was 5 mg/L) representing the synthetic polluted water at 20 ±2°C. The nitrates ions adsorption capacity of the three prepared materials was calculated with the formula:

$$Uptake = \frac{V \times (C_i - C_e)}{m} \quad (3)$$

where: Uptake - adsorption capacity at time t, the concentration of nitrates retained per unit mass of adsorbent materials (mg/L); V - volume of solution containing nitrate ions (mL); C_i - initial concentration of the nitrate ions (mg/L); C_e - equilibrium concentration (mg/L); m - adsorbent weight (mg).

In order to investigate the effect of pH on nitrate adsorption, the experiments were conducted in the 2-10 pH range. The pH of the water solution was adjusted using 0.1M HCl or 0.1M KOH.

3. RESULTS AND DISCUSSION

3.1. Characterization of prepared adsorbent material

The X-ray diffraction (XRD) shows the distorted spinel structure of γ -Al₂O₃ (Fig. 2). The characteristic diffraction peaks observed for bimetallic particles Pd-Sn are: 2 θ =38.50, 43.0. The average crystallite size calculated with the Scherrer formula was 40 nm.

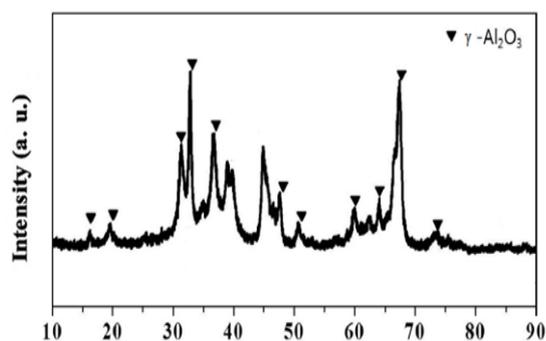


Fig. 2 - XRD for Pd-Sn/Al₂O₃

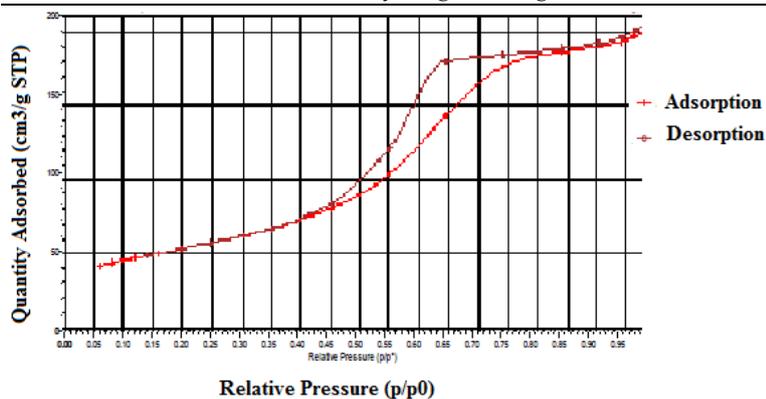


Fig. 3 - The adsorption-desorption isotherm of the Pd-Sn/ γ -Al₂O₃ material

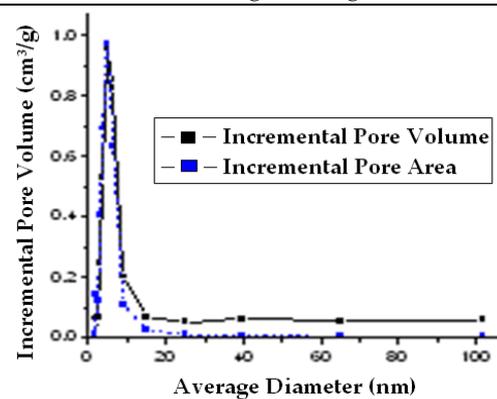


Fig. 4 - Pores size distribution of the material Pd-Sn/ γ -Al₂O₃

Based on figures 3 and 4 it could be observed that the specific surface area of the material is Pd-Sn/ γ -Al₂O₃ 275m²/g and the value of pores diameter is between 2 and 10 nm.

The TEM image from figure 5 indicates that the Pd-Sn/ γ -Al₂O₃ mean particle size is of 100 nm.

3.2. Nitrate ions adsorption study

In figure 6 was presented the plot adsorption of nitrate ions on Pd-Sn/ γ -Al₂O₃, nickel ferrite and nickel titanate used as adsorbent materials. Maximum adsorption capacity of nitrate was obtained at pH 3.5.

The maximum adsorption capacity values were 3.598 mg/L for Pd-Sn/ γ -Al₂O₃, 3.176 mg/L for nickel titanate and 3.051 mg/L for nickel ferrite. The adsorption

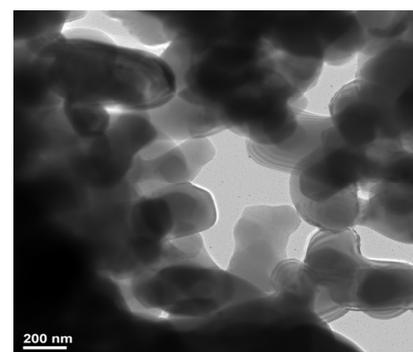


Fig. 5 - TEM image of Pd-Sn/ γ -Al₂O₃

equilibrium was obtained at pH = 3.5.

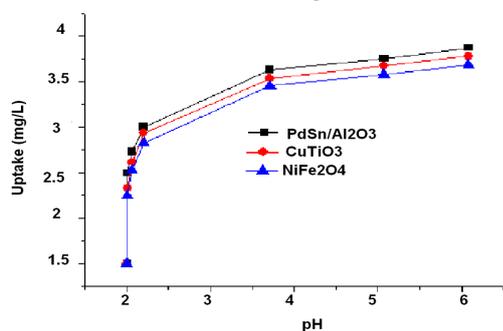


Fig. 6 - Adsorption plot for nitrate anions for Pd-Sn/Al₂O₃, NiTiO₃ and NiFe₂O₄

SIPS isotherm model

The SIPS isotherm model considers that the adsorption efficiency is limited at high concentration of ions in solution. The model is similar to the Langmuir isotherm, with the exception of a parameter representing heterogeneous system.

The SIPS model reduces to Langmuir's model when $\gamma = 1$.

$$Q_e = Q_{max} \times \frac{(K_s \times C_e)^\gamma}{1 + (K_s \times C_e)^\gamma} \quad (4)$$

where: Q_e – the total adsorption capacity at equilibrium (mg/L); Q_{max} – maximum adsorption capacity of the adsorbent material (mg/L); C_e – equilibrium concentration (mg/L); K_s – adsorption constant (dissociation parameter); n - number of variable parameters (3);

The following regression factors were obtained: 0.9987 for Pd-Sn/Al₂O₃, 0.9984 for NiTiO₃ and 0.9982 for NiFe₂O₄ (Fig.7). The regression factors show that the best results regarding nitrate ions adsorption were obtained for Pd-Sn/Al₂O₃ material. This fact could be explained based on the specific surface area values are of the three adsorbent materials: 275m²/g for Pd-Sn/ Al₂O₃, 32,6 m²/g for NiTiO₃ and 10,1 m²/g for NiFe₂O₄ [8].

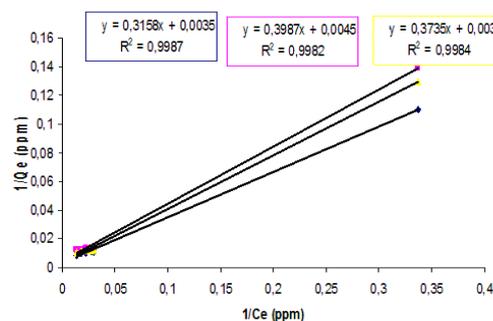


Fig. 7 - SIPS linear model representation for nitrate ions adsorption of onto Pd-Sn/Al₂O₃, NiTiO₃ and NiFe₂O₄

4. CONCLUSIONS

The experimental results of this study describe the adsorption capacity of Pd-Sn/Al₂O₃, NiTiO₃ and NiFe₂O₄ for nitrates removal from water. The results show that the adsorption effectiveness of Pd-Sn/Al₂O₃ for nitrate removal was higher in comparison with those of nickel titanate and nickel ferrite for a concentration of nitrate tested of 5 mg/L. The specific surface area and the pH values have influenced the adsorption capacity of the tested materials.

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