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Bio-synthesis of palladium nanoparticle using *Spirulina platensis* alga extract and its application as adsorbent

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ABSTRACT

In this study, the potential of *Spirulina platensis* alga for the production of palladium nanoparticles and their application for lead removal from aqueous solution was studied. The synthesized palladium nanoparticle characteristics were identified UV–visible, XRD, SEM, TEM and FTIR analyses. The palladium nanoparticles have spherical shape and size within the range of 10–20 nm. The adsorption experiments were conducted in batch system. The effects of certain parameters such as contact time, pH, adsorbent dose, and initial lead concentration on the adsorption process were investigated. The highest adsorption efficiency was obtained at pH 6, contact time 60 min, adsorbent dose 0.5 g/L, and lead concentration 10 mg/L. With increase in initial lead concentration from 10–150 mg/L, the removal percentage decreased from 87% to 32%, while as the adsorbent dose increased from 0.02 to 0.5 g/L, the removal percentage increased from 12% to 90%. Freundlich model compared to Langmuir model can better describe the adsorption behavior of lead with palladium nanoparticle. According to R^2 values (higher than 0.985), Freundlich isotherm model and pseudo-second-order kinetic model can better explain lead uptake by palladium nanoparticle than Langmuir isotherm model and pseudo-first-order kinetic model.

1. Introduction

Population growth and industrial development lead to environmental issues such as water pollution due to the discharge of industrial pollutants into bodies of water [1]. These pollutants are dangerous to human and other living organisms because of food chain accumulation [2]. Lead is one of the highly poisonous contaminant in water that WHO has set a limit (0.01 mg/L) for it (World Health Organization, 2008). Severe damage to the brain, kidneys, and gastrointestinal tract, especially in children are some of toxic effects of lead [3]. Lead contamination in water resources is generally caused by the wastewater of battery, dyeing, and food industries [4]. Several physical-chemical methods such as oxidation and reduction, sequestration, ion exchange, reverse osmosis, and evaporation have been used to remove heavy metals from wastewater [5–13]. These suffer from certain disadvantages including production of concentrated wastewater or waste materials and stupendous costs [14]. Therefore, it is necessary to develop modern methods to remove lead from contaminated waters.

Adsorption of metals using nanoparticles is one of the eco-friendly technologies that have recently been efficiently applied to remove heavy metals and other pollutants from water and wastewater [15]. Because of having small size, large specific surface area, crystalline form, unique network order, and high reactivity, nanoparticles can be used to treat and transform pollutants into less harmful substances [16]. Nano-sized metals or metal oxides such as ferric oxides [17,18], manganese oxides [18,19], aluminum oxides [18,20], titanium oxides [18,21], magnesium oxides [18,22], cerium oxides [18,23], and palladium [24] have been considered as adsorbent for heavy metals removal from aqueous solution. For example, Zhang et al. studied lead removal using zero-valent iron nanoparticles with kaolinite stabilizers, and found that K-nZVI was highly capable for removing lead from aqueous solutions [15]. Rajput et al. [25] investigated removal of lead and copper from aqueous solutions using superparamagnetic maghemite (γ-Fe_2O_3) nanoparticles. Cao et al. [23] synthesized CeO_2 nanocrystals via hydrothermal method and found to have an excellent adsorption capacity for heavy metal ions such as As (V), Cr (VI), Pb (II). Giammar et al. [26] studied the removal of lead from aqueous system using TiO_2 nanoparticles with different particle sizes and compositions.

Abbreviations: XRD, X-ray powder diffraction; SEM, Scanning electron microscopy; TEM, Transmission electron microscopy; FTIR, Fourier-transform infrared; WHO, World Health Organization; C_e, Equilibrium concentration; K_L, Langmuir constant; K_f, Freundlich constants; q_{max}, Maximum adsorption capacity; q_e, Equilibrium adsorption capacity; R^2, Correlation coefficient

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Ma et al. [27] found that the ZnO nanosheets had good adsorption capacity for lead ion owing to the role of surface hydroxy functional groups of ZnO. Nevertheless, few works have been conducted so far on the heavy metal adsorption on the palladium nanoparticles [28,29].

Biosynthesis of metal nanoparticles recently is taken into consideration because of abundant, cheap and renewable resources acting as metal reducing [30]. For the synthesis of palladium nanoparticles, biological materials such as plant parts [31], bark [32], peels [33], root [34], leaf [35–38], bacteria [39,40] and algae [24] have been used. *Spirulina platensis is* one of part of blue-green microalga (cyanobacteria) family that found in the tropical and subtropical lakes with high levels of carbonate and bicarbonate. Recently, this alga was used to biosynthesize of metal nanoparticles such as silver and gold [41,42].

In this research, we aim to assess the ability of *Spirulina platensis* to biosynthesis of palladium nanoparticle and their application for lead removal from aqueous system. The properties of as-prepared nanoparticle such as morphology, size, crystal structure and functional groups were identified with various technologies. In order to investigate the adsorption behavior of the nanoparticle, batch experiments was conducted. The effects of different parameters such as pH, adsorbent dose, initial lead concentration, and contact time on adsorption process were studied. To the best of our knowledge, this is the first research that describes the synthesis of palladium nanoparticles using *Spirulina platensis* extract and its use as lead adsorbent.

2. Materials and methods

2.1. Material

Palladium chloride ($PdCl_2$), lead nitrate ($Pb(NO_3)_2$, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck Company (Germany). Blue-green algae *Spirulina platensis* was cultured in the laboratory. The alga biomass was obtained by centrifuging at 3000 rpm for 20 min and then dried at 40 °C.

2.2. Preparation of the extract

To prepare extract, 1 g of dry biomass of *Spirulina platensis* was added to 100 mL of distilled water in 250 mL flask. The mixture was stirred at 60 °C for 20 min and then centrifuges at 3000 rpm. Finally, the obtained material was filtered and kept at 4 °C for further use.

2.3. Synthesis of palladium nanoparticles

10 mL of alga extract was added to 50 mL of 1 mM $PdCl_2$ solution at 70 °C at constant stirring. The color of the reaction mixture changed gradually from yellow to dark brown in 20 min, which indicated the formation of palladium nanoparticles.

2.4. Batch sorption experiments

All batch adsorption experiments were carried out on a mechanical shaker at 120 rpm in an Erlenmeyer flask. The first experiments were conducted to investigate the effect of the initial pH solution (2, 3, 5, 6, 7, and 9) on adsorption. The initial pH was adjusted using nitric acid and NaOH. 0.02 g of adsorbent was added to the metal solution and shake for 10 min. The second experiments were performed to investigate the effect of contact time on the removal process. The condition of these experiments was as follow: 50 mg/L lead concentration, 0.02 g adsorbent, pH 6 and contact time 10–120 min. The effect of adsorbent's dosage was evaluated in the third experiments. Different amounts (0.02, 0.04, 0.06, 0.08, 0.1, and 0.5 g) of adsorbent were introduced into the containers containing 100 mL of 50 mg/L of the lead solution. In the fourth experiment, the effect of initial metal concentration on adsorption process was studied. Different lead concentration (10, 20, 30, 50, 100, and 150 mg/L), pH 6, 0.2 g adsorbent were the experiment condition. All experiments were conducted in triplicate.

2.5. Adsorption calculations and modeling

The adsorbent's equilibrium capacity was calculated by following equation.

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e represents the amount of adsorbed metal ions per the adsorbent mass, C_e the equilibrium concentration (mg/L) of metal ions in the solution, V the solution volume (mL), and m the adsorbent mass (g). The percentage of metal removal was calculated according to Eq. (2):

$$U_P = 100 \times \left(\frac{C_e}{C_i}\right) \tag{2}$$

where C_i and C_e (ppm) display the initial and equilibrium metal concentrations, respectively.

The adsorption process was studied by Langmuir and Freundlich adsorption isotherms. Their Linearized isotherm equations are as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \left(\frac{C_e}{q_{\max}}\right) \tag{3}$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{4}$$

where C_e (mg/L) represents the equilibrium concentration, q_e (mg/g) is the adsorption capacity at equilibrium time, K_L is Langmuir constant, $q_{\max}$ (mg/g) is the maximum adsorption capacity, K_f and n are Freundlich constants.

The mechanism of adsorption lead by palladium nanoparticle was determined by the pseudo-first-order and pseudo-second-order models. Eqs. (5) and (6) represent their linearized forms.

$$\log(1 - q_t/q_e) = -\frac{K_1}{2.303}t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{6}$$

where t is time, K_1 and K_2 are kinetics equilibrium velocity constants.

2.6. Characterization of synthesized palladium nanoparticles

The synthesized palladium nanoparticles were measured using UV – visible spectrophotometer (DR 5000, HACH, USA) in the wave number range 200–600 nm. The X ray diffraction (XRD) analysis was performed using an X-ray diffractometer (X'Pert Pro, PANalytical, Holland) in the scanning range (2θ) of 30–90°. The instrument worked at a voltage of 40 kV and a current of 30 mA with monochromatic Cu Kα radiation. Fourier-transform infrared spectroscopy (FTIR) (IRAffinity-1S, Shimadzu, Japan) was applied to specify different functional groups on alga extract and palladium nanoparticles. Transmission electron microscopy (TEM) images were gotten by an electron microscope (CM120, Philips, Holland) at an accelerating voltage of 120 kV. For TEM analysis, a drop of the aqueous suspension was poured onto the carbon coated copper grids and then evaporating prior to measurement.

3. Results and discussion

3.1. Adsorbent characteristics

The biosynthesis of palladium nanoparticles with *Spirulina platensis* algae was monitored first visually and then UV–visible spectroscopy.