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Microwave-assisted functionalization of *Rosa Canina-L* fruits activated carbon with tetraethylenepentamine and its adsorption behavior toward Ni(II) in aqueous solution: Kinetic, equilibrium and thermodynamic studies

Maryam Ghasemi [a], Mohammad Zeinaly Khosroshahy [b], Arash Bavand Abbasabadi [c], Nahid Ghasemi [f], Hamedreza Javadian [d,*], Mehdi Fattahi [e]

[a] *Young Researchers and Elite Club, Arak Branch, Islamic Azad University, Arak, Iran*
[b] *Faculty of Food Science and Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran*
[c] *Department of Chemical Engineering, Faculty of Engineering, University of Tehran, Tehran, Iran*
[d] *Department of Chemical Engineering, Shahrood Branch, Islamic Azad University, Shahrood, Iran*
[e] *Technical Inspection Engineering Department, Petroleum University of Technology, Abadan, Iran*
[f] *Department of Chemistry, Sciences Faculty, Arak Branch, Islamic Azad University, Arak, Iran*

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ABSTRACT

This paper investigates the ability of the tetraethylenepentamine-functionalized *Rosa Canina-L* fruits activated carbon (TEPFRCA) prepared by microwave-assisted technique to remove Ni(II) from an aqueous solution. The activated carbon was prepared by concentrated H_2SO_4 and was characterized using the FE-SEM, FTIR and N_2 adsorption–desorption isotherms. The batch method was performed by varying the contact time (0–60 min), initial metal ion concentration (50–500 mg/L), temperature (298–333 K), adsorbent dose (0.05–0.15 g) and initial pH (2–8) of the solution. The adsorption process follows pseudo-second-order reaction kinetics. The equilibrium data were fitted well by the Langmuir and Freundlich model. The monolayer adsorption capacities were found to be 128.205, 135.135 and 140.845 mg/g at 298, 318 and 333 K, respectively. Thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ were also calculated. The adsorption of Ni(II) on TEPFRCA was found to be spontaneous and endothermic under standard conditions. The positive value of $\Delta S°$ showed that Ni(II) adsorption caused the randomness in the system. The maximum Ni(II) recovery efficiencies were 65.1% and 62.7% for 0.1 HNO_3 and 0.1 HCl, respectively. The results showed that TEPFRCA can be used as a low cost adsorbent for the removal of Ni(II) from aqueous solutions.

1. Introduction

Heavy cations are elements with a specific gravity greater than 5.0 and an atomic weight ranging between 63.5 and 200.6. In developing countries where industries such as metal plating, mining, tanning, and the manufacturing of fertilizers, batteries, paper and pesticides are growing, it is common for wastewaters containing heavy cations to be expelled into the environment [1]. Heavy cations are not biodegradable and tend to cumulate in living organisms. Many heavy cations are toxic and may contain carcinogenic elements. Toxic heavy cations found in industrial wastewater include zinc, copper, nickel, mercury, cadmium, lead, and chromium [2].

Various methods are used to remove heavy cations including adsorption, biosorption, chemical precipitation, electrochemical treatments, ion-exchange, and membrane filtration. Adsorption and biosorption are flexible designs and they produce a high-quality, treated effluent. The adsorption process is frequently reversible as adsorbents can be regenerated using a desorption process [3].

A high level of nickel may cause lung and kidney damage as well as gastrointestinal distress, pulmonary fibrosis and dermatitis [4]. Nickel is also a recognized human carcinogen. Different types of adsorbents have been used to remove nickel ions including almond husk activated carbon [5], kaolinite [6], sugar beet pulp [7], cloths activated carbon [8], peanut hulls [9], modified chitosan [10] and crab shells [11]. Researchers continue to find new, more effective adsorbents suitable for removing harmful nickel ions [12].

One of prevalent adsorbents which is usually used to remove metal from aqueous media is active carbon due to having particular surface and reusing properties, supreme porous structure, environmentally benign nature and minimum costs [13]. Preparations of activated carbons have been done from various types of materials due to

* Corresponding author. Tel.: +98 911 3235538.
E-mail address: hamedreza.javadian@yahoo.com (H. Javadian).

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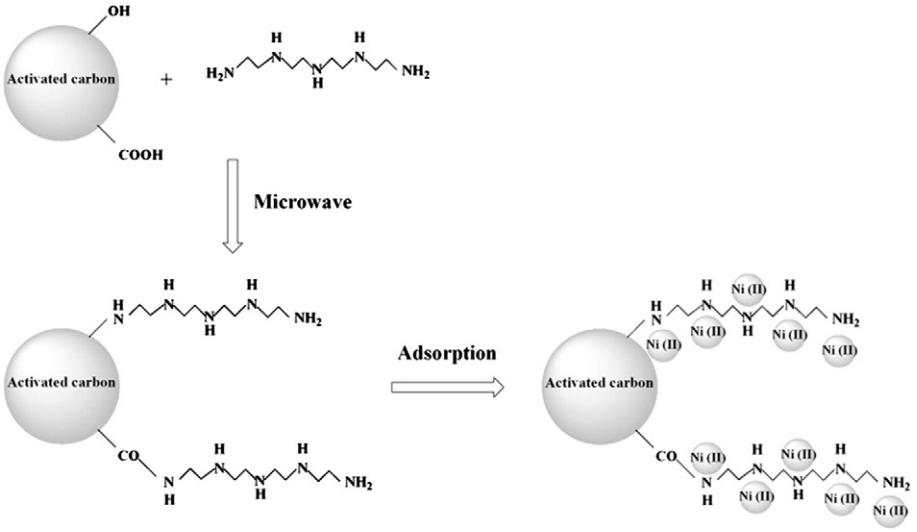

Scheme I. The pathway leading to the synthesis of the TEPFRCA and the possible mechanism of Ni(II) sorption.

existence of a large number of raw materials and from batch to batch the specifications of the activated carbon got very much. Chemical property of activated carbon is mainly determined by its carboxylic, lactonic and phenolic groups as organic functional groups which are included of heteroatoms such as O, N or S [14]. Functionalization of adsorbent with functional groups such as phosphate, hydroxyl, carboxylate, amide and amino groups can be one of the best methods which has been used by many researchers to improve sorption properties. It is well demonstrated that the formation of complex combinations of heavy metals via surface chelation mechanisms can be the reason of removing heavy metals [15]. Synthesis and modification of materials using microwave radiation have attracted considerable attention as a green technology. Microwave radiation has both electrical and magnetic properties [16]. Microwave heating generates efficient internal heat-transfer by penetrating subjects and causing uniform energy distribution throughout the material irradiated, which leads to an even chemical reaction. This is an advantage of microwave irradiation not achieved by indirect heating methods [17].

Rosa Canina-L is a species of wild rose found in Europe, Northwest Africa, and Western Asia. The plant is high in antioxidants, vitamins A, C, and E, flavonoids, and other bio-active compounds. *Rosa Canina-L* is currently being studied for its ability stop the growth of cancer cells and decrease cancer rates. Its fruits activated carbon can be functionalized with amine groups to use in environmental problems such as heavy metals removal from aqueous solutions.

The primary purpose of this paper was to remove Ni ions from aqueous solution using tetraethylenepentamine-functionalized *Rosa Canina-L* fruits activated carbon (TEPFRCA) prepared by microwave-assisted technique. The adsorbent was characterized using FE-SEM, FTIR and N_2 adsorption–desorption isotherms. The effects of several operating parameters such as contact time, initial Ni(II) ion concentration, temperature, pH and adsorbent dosage were studied to obtain the optimum conditions of adsorption process. Despite any faults incorporated in this study, it is the hope of the author that it will provide a basis for further research on *Rosa Canina-L* as a valuable plant.

2. Materials and methods

2.1. Materials

All chemicals used in this study were of analytical reagent grade purchased from Merck, Germany. To prepare a stock solution containing 1000 mg/L of Ni(II), $Ni(NO_3)_2.6H_2O$ was employed. The stock solution was diluted with deionized water to the desired Ni(II) concentrations.

2.2. Preparation of Rosa Canina-L fruits activated carbon (RCA)

For the preparation of activated carbon, 50 g of collected *Rosa Canina-L* fruits from Mazandaran, Iran, was air-dried, crushed and impregnated with concentrated H_2SO_4. Then, the materials were activated in a hot air oven at 150 °C for 24 h. The carbonized material was washed with distilled water and the activated carbon was immersed in a 1% $NaHCO_3$ solution to remove any remaining acids before it was washed again with distilled water until the pH of the activated carbon reached 6.5 [18]. Afterwards, it was dried in program controller at 105 °C for 24 h. A uniform particle size of 0.125 mm was obtained using a sieve.

2.3. Preparation of tetraethylenepentamine-functionalized Rosa Canina-L fruits activated carbon (TEPFRCA)

3.5 g of RCA was mixed with a 50 mL of solvent containing deionized water, ethanol or toluene and stirred for 30 min. 2.5 g of tetraethylenepentamine was then added to the mixture and the mixture was sonicated for 10 min. The mixtures were then heated under microwave irradiation (LG, WD700, 2450 MHz) with output power of 500 W for 20 min. The prepared sorbent was washed with Milli-Q water until the pH of the supernatant became neutral. The prepared sorbent was dried for 48 h at 50 °C and used for further study. Synthesis route scheme for TEPFRCA and sorption of Ni(II) are represented in Scheme I.

2.4. Instruments

The structure of the RCA and TEPFRCA was examined using the field emission scanning electron microscope (FE-SEM) (Hitachi-S4160, Japan) under an acceleration voltage of 20 kV with a high resolution of 3.0 nm. Organic functional groups were determined by FTIR spectroscopy (Shimadzu-8400S, Japan) in the wavelength of 4000–400 cm^{-1}.

BET surface area, total pore volume and pore diameter distribution was measured by Brunauer–Emmett–Teller (BET) method at liquid nitrogen temperature (−196 °C) using conventional gas adsorption apparatus (Belsorp-Mini II, Bel, Japan).