

Pb (II) Ion Removal from Aqueous Solutions by Adsorption Using Polypyrrole/Poly (Para Nitroaniline)/Poly (Para Hydroxyaniline) Applications of Composites in Soil Technology

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Abstract. *The efficiency of employing polypyrrole, poly(p-nitroaniline), and p-hydroxyaniline as adsorbents to remove lead (Pb^{2+}) ions from aqueous solutions is examined in this work. These functionalized chemicals and conducting polymers have active binding sites and a large surface area, which improves their capacity to absorb heavy metal ions. The study looks at a number of variables that affect adsorption efficacy, such as adsorbent dosage, initial Pb^{2+} concentration, pH, and contact time. The results reveal that all three materials have a great deal of potential for removing Pb^{2+} ions, while their efficiency varies according to their surface characteristics and chemical makeup. The results imply that these substances may hold promise for heavy metal-contaminated wastewater treatment applications.*

Key words: *Adsorption, polymers, wastewater.*

1. INTRODUCTION

Large molecules known as polymers are composed of monomers, which are repeating structural units. They might be manmade, like nylon and plastic, or natural, like proteins and cellulose. Because of their strength, low weight, and adaptability, polymers are employed extensively ^{[1] [2]}

Chemical elements with a high atomic weight and density are known as heavy elements, or heavy metals. They usually consist of elements such as uranium (U), arsenic (As), cadmium (Cd), lead (Pb), and mercury (Hg). Although these elements are found naturally in the crust of the Earth, human activities like mining, manufacturing, and farming can greatly raise their concentration in the environment.

Heavy elements can have both beneficial and detrimental effects. Certain elements, such as iron and zinc, are required in tiny levels for biological functions, yet many are poisonous to living beings at excessive doses. They can accumulate in the body over time and lead to illnesses like cancer, neurological conditions, and organ damage ^[3,4,5,6].

Heavy elements are a significant problem for environmental pollution and public health because of their persistence and possible toxicity. Monitoring, controlling, and limiting their release into ecosystems are continuing global initiatives. ^[7,8]

2. MATERIALS AND METHODS

2.1 Raw Materials

Para- hydroxy aniline, pyrrole and Ethanol (sigma Aldrich), Hydrochloric acid (BDH), Sodium dodecyl sulphate (CDH), Aluminum hydroxide (Merck), Nitrogen Gas (Industrial), Potassium Persulfate (CDH).

2.2 Synthesis of Poly para-hydroxyaniline

1g of para hydroxy aniline was dissolved in 50 ml of HCl [0.1M] to create P(p-OH An). The mixture was maintained at 5°C. [9,10]. The solution was filtered and periodically washed with deionized water to provide a glossy dark finish when the churning was stopped for an hour [11]. In order to improve doping, it was cleansed with 3 milliliters of hydrochloric acid and 100 milliliters of ionized water before being dried in an oven at 40 to 50 degrees Celsius. °C [12].

2.3 Synthesis of poly pyrrole

The synthesis of PPy is outlined as follows: Initially, 1M HCl was added to a 200ml beaker with stirring, followed by the dropwise addition of chilled APS solution. Subsequently, 4 ml of pyrrole monomer was added dropwise to initiate polymerization. The mixture was then stirred for approximately 4 hours until the formation of a precipitate. The solution was stored overnight in a refrigerator. It is important to note that the temperature was kept between 0 to 5 °C and the pH was maintained at around 2 during the reaction. The mixture was then filtered through a Buchner funnel and cleaned with ethanol, acetone, and distilled water. After obtaining a black precipitate, it was dried at 80 °C in an oven. In the end, an amorphous black powder was obtained as the intended PPy result. [13]

2.4 Synthesis of p-nitroaniline

P(p-OH An) was created by dissolving one gram of para hydroxy aniline in fifty milliliters of HCl [0.1M], keeping the solution at five degrees Celsius, and then preparing a second solution by dissolving one gram of KIO₃ in fifty milliliters of HCl [1M] and mixing it with the first solution (para hydroxy aniline with HCl) using a magnetic stirrer. For two hours, the first solution is continually mixed while the second solution (KIO₃ with HCl) is added drop by drop. The mixture is kept at five degrees Celsius for the second day and then stirred again for four hours. After stopping the stirring of the solution for an hour, it was filtered and repeatedly cleaned with three milliliters of hydrochloric acid that had been mixed with ionized water to increase doping. Lastly, it was dried at 40 to 50 degrees Celsius in an oven. [14]

2.5 Synthesis of poly (polypyrrole-poly p-hydroxy aniline poly p-nitro aniline

Using an ultrasonic instrument, For thirty seconds, One hundred milliliters of 0.1 M HCl were used to dissolve one gram of pyrrole. One gram of para-hydroxyaniline was then dissolved in fifty milliliters of 0.1 M HCl. Next, 50 milliliters of 0.1 M HCl were used to dissolve one gram of 0.1 M potassium persulfate. After that, the first solution was mixed with the third solution, para-nitroaniline, and allowed to sit for fifteen minutes. After that, two hours were spent waiting for a black precipitate to form before adding the second solution to the third. Filtration was then used to separate the precipitate from the filtrate. After being repeatedly cleaned with ethanol and water, the precipitate was dried for two hours at 60 °C in a lab oven [15].

2.6 Preparation of Standard Solutions and Analytical Method:

Standard Solutions

For the purpose of conducting analytical studies, the weights shown in Table (1) were used, and then Reserve standard solutions were prepared at a concentration of (1000 ppm) and were called storage solutions. (Solution Stock) Ions of the elements used in the study, which are (pb⁺²) (From there, other standard solutions were prepared with a concentration of 100 parts per million (100 ppm) This is done by diluting certain volumes of standard reserve solutions with a concentration of (1000 ppm), where deionized distilled water was used all preparation processes [16]

Table (1): Shows The Weight Used for The Compound

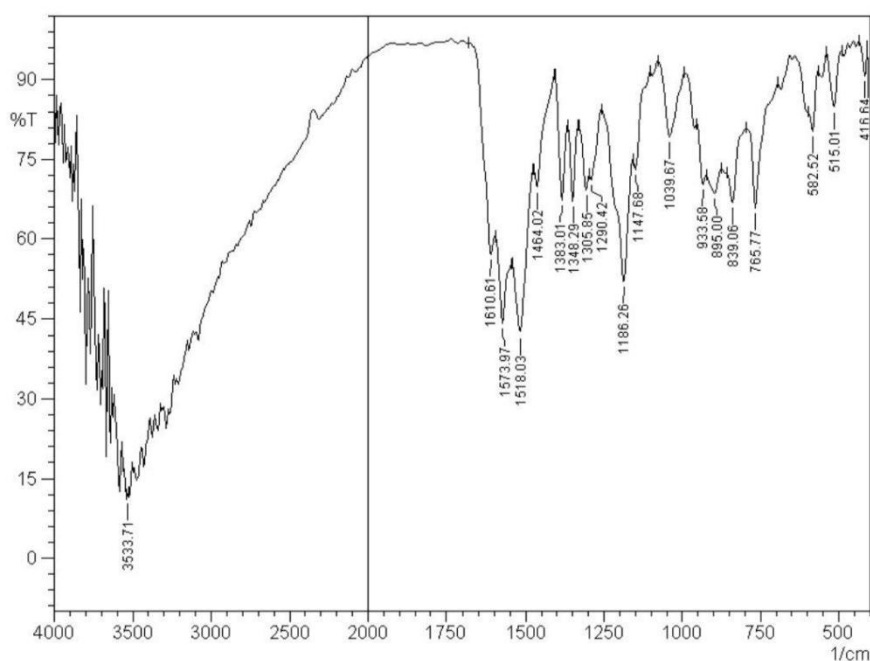
Metal	Molecular Formula	Molecular Weight	The Weight
Aqueous Lead Nitrate	$\text{pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	439.316	4.393 g

Analytical Measurement:

In this study, the meal method was used, which involves treating a specific weight of resin Study with specific volumes of solutions of the elements that are studied in this research in acid functions Specific and different time periods depending on the type and nature of the study, after which the solutions are filtered It is separated from the resin, and then the concentration of the remaining ions in the filtrate is determined by using Flame atomic absorption device, and thus through this method it is possible to determine the workability of the resin The method used in this study depends on the ions used in the research This method is summarized as follows Weigh (0.1 gm) of the prepared resin and put it in 10 ml volumetric bottles and add It has 10 ml of ion at a ppm concentration of 100 and at acid functions (1, 3, 5,7), then Volumetric bottles are placed in a water bath device equipped with a vibrator and a temperature regulator at a rate 120 r/min and at a temperature of 25 C° With different and specific time periods, 10 minute , 30 minute , 60 minute , 90 minute , 120 minute , 150 minute After completion, the solutions were filtered and the concentration was calculated. The remaining ion in the filtrate solution using atomic absorption technology Atomic absorption without flameless^[17,18].

3. Results and Discussion:**3.1 FT-IR Spectra of poly pyrrole / poly p-hydroxy aniline /poly p-nitro aniline**

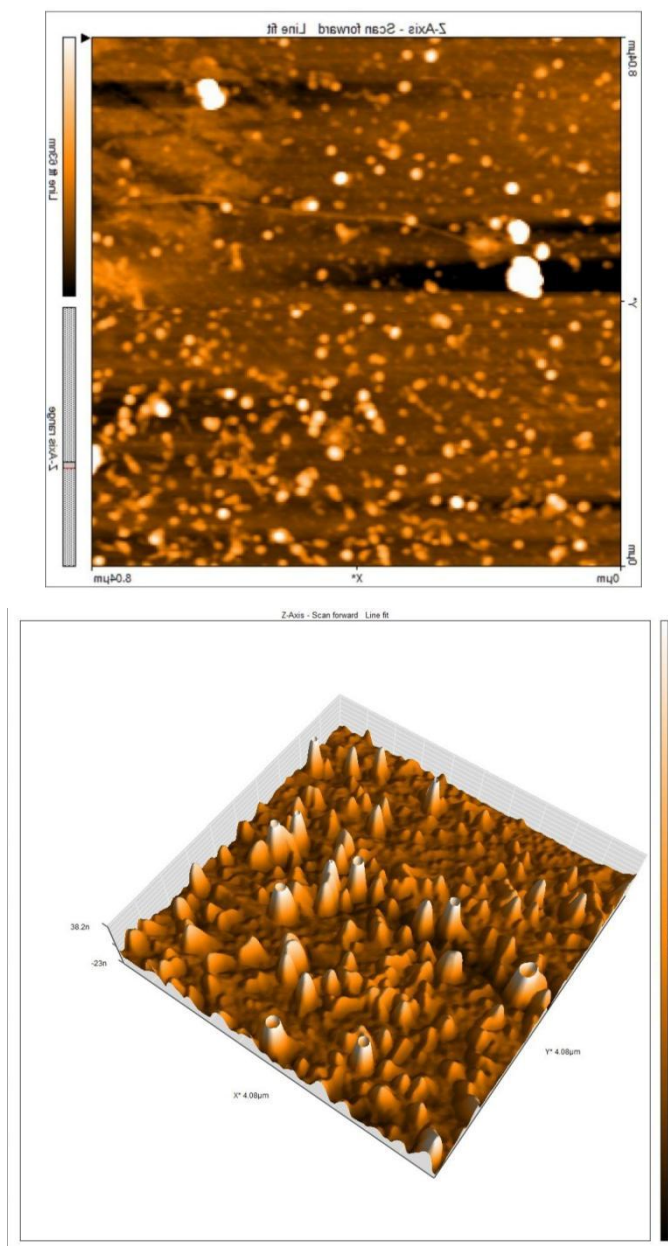
The wave number 3533.71cm^{-1} in Figure (1) indicates the state of the O-H group. cm^{-1} . The absorption bands at wave numbers 1610.61cm^{-1} , 1573.97cm^{-1} , 1518.03cm^{-1} , reflect the condition of the Polypyrrole group that has been successfully peak at 1464.02cm^{-1} showed a decrease in the sharpness of the absorption peak, which suggested that PPy had been successfully. The absorption bands at wave numbers 933.58cm^{-1} , 895.00cm^{-1} , and 839.06cm^{-1} reflect the C=C group.^[19]

**Figure (1): FT-IR of poly pyrrole / poly p-hydroxy aniline /poly p-nitro aniline**

1573.97cm^{-1} , 1464.02cm^{-1} , 1348.01cm^{-1} , 1348.29cm^{-1} and 1305.85cm^{-1} This can be attributed to the different metal oxides included in the composite. The O-H phenolic group in the nanocomposite is represented by the wide peaks at $3200\text{--}3500\text{cm}^{-1}$.^(20,21,22)

3.2 The AFM of Photographs of poly pyrrole/ poly hydroxyaniline/ poly nitro aniline

For AFM characterization, the magnetite nanoparticles were applied to the glass and allowed to dry. The information was gathered to ascertain the samples' roughness and three dimensions (3D). The generated three-dimensional images of the sample are displayed in Figure (2,3). the particles is around nm, and their diameter is 120.58 nm for the scanned area of one by one^{[19] [20]}.



Calculation Thermodynamic Functions:

Table (1): Shows the values of thermodynamic equilibrium constants at different temperatures ^{(21)[22]}

T(K)	ΔG°	ΔH°	ΔS°
298	40.877	33.773	-187.708
313	55.888		
323	54.895		

The in situ immobilization of heavy metals using a chemical amendment is one remediation technique that is both economical and environmentally safe by reducing the mobility and availability of metals. Soils contaminated with metals, radionuclides, other inorganic contaminants, and non-or semi-volatile organic molecules are the best for stability and solidification. For the 57 categories of hazardous wastes specified in RCRA, USEPA has determined that S/S is the best demonstrated

available technology (BDAT) . About 25% of Superfund remediation sites in the USA were treated by S/S technologies as opposed to other technologies (USEPA). Currently, a range of products with the highest lead value, including lime, organic waste, calcium carbonate, and bone meal, have an efficiency of 30 to 80% .^{(23) (24) (25)}

References:

1. Odian, G. (2004). Principles of polymerization. John Wiley & Sons.
2. Namazi, H. (2017). Polymers in our daily life. BioImpacts: BI, 7(2), 73.
3. Rasha Jasim; Thesis "New polymeric corrosion inhibition for carbon steel", College of Science, University of Thi-Qar, (2021)
4. Legrand, P., Lesieur, S., Bochot, A., Gref, R., Raatjes, W., Barratt, G., & Vauthier, C. (2007). Influence of polymer behaviour in organic solution on the production of polylactide nanoparticles by nanoprecipitation. International journal of pharmaceutics, 344(1-2), 33-43.
5. Chandrasekhar, V., Thilagar, P., & Pandian, B. M. (2007). Cyclophosphazene-based multi-site coordination ligands. Coordination Chemistry Reviews, 251(9-10), 1045-1074.
6. Karen I. Winey and Richard A. Vaia, al. Research gate, Vol. 32, pp.10.1557, (2007)
7. Zhang, K., Park, B. J., Fang, F. F., & Choi, H. J. (2009). Sonochemical preparation of polymer nanocomposites. Molecules, 14(6), 2095-2110.
8. Tawfik, E. K. M. (2013). Radiation effect on characterization and physical properties of polymer nano composites.
9. McWilliams, A. (2006). Nanocomposites, nanoparticles, nanoclays, and nanotubes. NANO21C, BCC Research, Norwalk, CT.
10. Oliveira, M., & Machado, A. V. (2013). Preparation of polymer-based nanocomposites by different routes.
11. Uddin, A. J. (2010). Coatings for technical textile yarns. In Technical Textile Yarns (pp. 140-184). Woodhead Publishing.
12. Chen, A., Wang, H., Zhao, B., & Li, X. (2003). The preparation of polypyrrole-Fe₃O₄ nanocomposites by the use of common ion effect. Synthetic Metals, 139(2), 411-415.
13. Chen, A., Wang, H., Zhao, B., & Li, X. (2003). The preparation of polypyrrole-Fe₃O₄ nanocomposites by the use of common ion effect. Synthetic Metals, 139(2), 411-415.
14. Nosheen, S., Irfan, M., Habib, F., Abbas, S. Z., Waseem, B., Iftikhar, F., ... & Aziz, A. K. (2020). Synthesis and characterization of polypyrrole synthesized via different routes. Int. J. Eng. Res. Technol., 9(6), 1630-1633.
15. Abed, A. S., Ziad, K. M., & Abdullah, A. Q. (2015). Synthesis and Study Some Optical Properties of Conducting Polymer Poly p-Anisidine (PPANS) Doped with Camphor Sulphonic Acid (CSA). basrah journal of science, 33(1A), 137-155.
16. Sun, J., Zhou, S., Hou, P., Yang, Y., Weng, J., Li, X., & Li, M. (2007). Synthesis and characterization of biocompatible Fe₃O₄ nanoparticles. Journal of biomedical materials research Part A, 80(2), 333-341.
17. Mai, H. D., Rafiq, K., & Yoo, H. (2017). Nano metal-organic framework-derived inorganic hybrid nanomaterials: synthetic strategies and applications. Chemistry—A European Journal, 23(24), 5631-5651.
18. Zhang, L., & Lian, J. (2007). Electrochemical synthesis of copolymer of aniline and o-aminophenol and its use to the electrocatalytic oxidation of ascorbic acid. Journal of electroanalytical Chemistry, 611(1-2), 51-59.

19. Waly, Z. S., & Merdas, S. M. (2024). Magnetic Nanocomposites Revolutionize Heavy Metal Adsorption for Environmental Cleanup. *Academia Open*, 9(2), 10-21070.
20. Li, B., Weng, X., Wu, G., Zhang, Y., Lv, X., & Gu, G. (2017). Synthesis of Fe₃O₄/polypyrrole/polyaniline nanocomposites by in-situ method and their electromagnetic absorbing properties. *Journal of Saudi Chemical Society*, 21(4), 466-472.
21. V.G. Kulkarni, L.D. Cambell, W.R. Mathew, Thermal stability of polyaniline. *Synth. Met.* 30, 321 (1989).
22. Alibrahimi, Ahmed A., and W. O. Toamah. "Removing metal ions of cobalt (II) from aqueous solutions by CaO nanoparticle." *Journal of Physics: Conference Series*. Vol. 1279. No. 1. IOP Publishing, 2019.
23. Derakhshan Nejad, Zahra, Myung Chae Jung, and Ki-Hyun Kim. "Remediation of soils contaminated with heavy metals with an emphasis on immobilization technology." *Environmental geochemistry and health* 40.3 (2018): 927-953.
24. Joseph, Lesley, et al. "Removal of heavy metals from water sources in the developing world using low-cost materials: A review." *Chemosphere* 229 (2019): 142-159.
25. Azhar, Umair, et al. "Remediation techniques for elimination of heavy metal pollutants from soil: A review." *Environmental research* 214 (2022): 113918.