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Characterization of Copper Entrapment to Polystyrene as an Adsorber for Wastewater Remediation Application

Nur Aimi Syafika Mohd Radzi¹, Arif Agam^{2*}

^{1, 2} Faculty of Applied Sciences and Technology, Universiti Tun Hussein Onn Malaysia (Pagoh Campus), 84600 Pagoh, Muar, Johor, MALAYSIA.

*Corresponding Author Designation

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Abstract: Among hazardous materials released by industrial activities are heavy metals and the cost to create a cheaper absorber to purify wastewater from industries has become the major trend in research. Due to their simplicity, low cost, high reactivity, low toxicity, and chemical stability, numerous semiconductors such as ZnO, ZnS, CdS, TiO₂, MoO₃, Ag₂O, and Fe₂O₃ are used to degrade toxic organic pollutants or act as absorbers for heavy metals removal from wastewater, either through photocatalytic processes or chemical reduction. In this research, Expanded Polystyrene (EPS) is used as the base material, trapping Cu nanoparticles (Cu NPs) in absorbing Zn heavy metals in the wastewater. Cu NPs were synthesized by preparing the stock solution of CuSO₄.5H₂O and the same goes for the preparation of Zn synthetic wastewater. As a sample for wastewater, stock solutions of Zn synthetic wastewater were synthesized at concentrations of 10, 20, and 30 mg/l. EPS was synthesized by the nanoprecipitation method by using Tetrahydrofuran (THF) as the reducing agent. The chemical interaction of PS Cu NPS was determined by Fourier Transform Infrared Spectroscopy (FTIR) while the surface morphology of each of the samples was determined by Field Emission Scanning Electron Microscopy (FESEM). UV-Vis was utilized to measure the absorbance value of Zn. The removal of Zn heavy metals was influenced by two parameters: pH value and adsorber adsorbent dose. By 45 minutes, PS Cu NPs had removed more than 60% of Zn heavy metals from synthetic wastewater. The optimal Zn absorption by PS Cu NPs for both pH levels and adsorbent doses were 64% at pH 5 and 56% at 0.04 g of adsorbent dosage, respectively. This paper identifies PS Cu NPs as a potentially useful nanotechnology material capable of removing heavy metals from wastewater remediation applications.

Keywords: Adsorption, Heavy Metal, Expanded Polystyrene, Wastewater

1. Introduction

One of the most urgent problems in the globe is the rapid rise of urbanization and industrialization, which dangerously contaminates groundwater and surface water [1]. The main source of heavy metal pollution in wastewater is the discharge of wastewater from businesses such as metal plating, leather tanning, textile dyeing, paint and pigment manufacture, batteries, fertilizer production, water cooling, and many more [2]. As industrial and human activities have grown rapidly, heavy metals have become more prevalent in wastewater. Thus, even though these heavy metals have no biological purpose, their toxic effects are still present in some of the other forms that are harmful to the human body and its proper functioning.

The primary sources of Zn entering the environment include wastewater discharged from several industrial sectors and Zn is often found in soil and water bodies [3]. Zn is essential for cellular processes in all living creatures. Zn not only minimizes the hazardous levels of different metals, but it also promotes plant growth features by limiting heavy metal uptake in plant sections [4]. Zinc is one of the most precious and widely utilized metals in industry. The primary focus of nanotechnology is on nanoscale dimensions or nanoparticles, where a large surface area to volume ratio results in strong binding sites. It increases the rate of absorption, particularly for heavy metals in wastewater [5]. Due to their high surface area to volume ratio, exceptional mechanical capabilities, and biocompatibility due to their polymer matrix, metal nanocomposites embedded in polymers (PS-MNCs) have the potential to be absorbent for heavy metals [5].

As a result, several technologies or methods for removing heavy metals in wastewater treatment applications, such as filtration, absorption, and advanced oxidation processes, have been developed. Adsorption has been widely used for heavy metal-infested wastewater treatment because of its operational simplicity, sludge-free operation, and adsorbent reuse potential in long-term applications [6]. The overall objectives of this research are to focus on synthesizing polystyrene embedded with Cu nanoparticles (PS Cu NPs), characterization of the samples using FTIR, FESEM and UV-Vis and study the adsorption analysis of Zn heavy metals.

2. Materials and Methods

The copper sulphate pentahydrate (CuSO₄.5H₂O) and zinc sulphate heptahydrate (ZnSO₄.7H₂O) used in this experiment are analytical chemical reagents. The experiment will begin by preparing the stock solution of CuSO₄.5H₂O and zinc synthetic wastewater. About 39.28 mg of CuSO₄.5H₂O and 43.97 mg of ZnSO₄.7H₂O was added in a two different 1000 ml volumetric flask containing 1000 ml of distilled water respectively. The solution was stirred for 10 min at 300 rpm to complete the reaction which means dissolving the chemical reagent. The expanded polystyrene (EPS) was synthesized via nanoprecipitation method. The sample solution was created by combining 10 ml of EPS and 30 ml of Cu NPs in an ultrasonic cleaning machine for 1 hour. These solutions were dropped onto the silicon substrate and allowed to evaporate for 24 hours at room temperature for FESEM: sample morphology, FTIR: chemical bonding analysis, and UV-Vis spectroscopy: Zn absorption study.

Batch adsorption experiments were investigated using two different parameters which are pH value and different adsorbent dosages. The experiment was carried out in 3 reagent bottles using different adsorbent dosages. Three different masses of EPS which are 0.02 g, 0.03 g and 0.04 g were weighed out using analytical balance respectively. Batch mode analysis was done by using a hot mechanical stirrer at fixed 150 rpms and 25°C. pH values of 2,3 and 5 were adjusted by adding a few drops of NaOH 1.0 M and HCL 1.0 M respectively into the concentration of 10,20 and 30 mg/l of Zn solution.

3. Results and Discussion

3.1 EPS embedded with Copper nanoparticles

The samples' morphology was examined using FESEM. The samples were examined for nanoparticle grain size and surface morphology. Figure 1 below illustrated FESEM micrographs of Cu doped with EPS at various adsorbent dosages. It was observed that nanoparticles of various sizes were forming [7]. The sample of 2% of EPS embedded with Cu nanoparticles shows bright and ball-liked nanoparticles and the particles were considered polystyrene. The PS-Cu NPs are made possible by the heterogeneous distribution of Cu nanoparticles in the EPS, which are tiny enough to fit inside the EPS cores. Figure 1 (b) illustrates the inhomogeneous structure induced by the presence of nanoparticles. Since the nanoparticle dispersion is more characterized by a variety of particle sizes and degrees, the deformation of the nanoparticles is not uniform and even. The surface morphology seen in Figure 1 (c) is a grapefruit-like structure of nanoparticles. In comparison to Figures 1 (a) and (b), the nanoparticles in the micrograph are quite dense. Because of the presence of Cu NP binding sites, several cracks were discovered along with the agglomerations, and the attraction to its neighbouring particles was strong. The addition of EPS to the CuSO4.5H2O resulted in a change of alteration in the morphology of PS Cu NPs. The average grain size as measured from FESEM images was 1.358 µm, 1.499 µm and 1.730 µm for 2%, 3% and 4% of CuSO_{4.5H2}O doped with EPS respectively. This method displays a heterogeneous size range and monodispersed distribution. From the evidence of the FESEM data, it concluded that the various EPS adsorbing doses utilized have an impact on the nanoparticles' size and morphology.



(a) 2%



(b) 3%



(c) 4%

Figure 1: FESEM micrographs of a) 2%, b) 3% and c) 4% of EPS embedded with CuSO₄.5H₂O

Each of the PS Cu NPs' chemical characteristics were evaluated using FTIR. Figure 2, 3 and 4 below shows that there is a broad peak observed at 3335.1 cm⁻¹, 3343.5 cm⁻¹ and 3340.7 cm⁻¹ respectively. The intermolecular hydrogen bond of the O-H stretching vibrations is represented by these three bands. The three peak band that exists at 1636 cm⁻¹, 1641.5 cm⁻¹ and 1636 cm⁻¹ in Figures 2, 3

and 4 were also shown respectively. The existence of aliphatic C-H deformation vibrations and carbonyl stretch, known as the amide group, causes the peak band to occur [8]. This peak exhibited Cu NPs characteristics, with Cu NPs production embedded in a matrix of PS Cu NPs. The presence of PS was shown at the very small peak of 1045.3 cm⁻¹ as it has the smallest value of PS which is 2% compared to another spectrum. 1040.8 cm⁻¹ observed in Figure 3 and 1042.5 cm⁻¹ observed in Figure 4 which corresponds to a deformation of aromatic C-H bending [9]. These results demonstrated that while the spectrum of different Cu NP doses changed much of the chemical bonding that exists in PS Cu NPs, the polymer-kind chemical bonding remained.



Figure 2: FTIR spectrum of 2% of EPS embedded Cu nanoparticles



Figure 3: FTIR spectrum of 3% of EPS embedded Cu nanoparticles



Figure 4: FTIR spectrum of 4% of EPS embedded Cu nanoparticles



3.2 Absorption analysis

Figure 5: The effect of pH values of Zn heavy metals

Figure 5 above shows the data removal efficiencies of Zn heavy metals against pH values by varying the concentrations of Zn heavy metals at 10,20 and 30 mg/l. The result shows that the percentage of heavy metal increase from lower pH which is 2 until maximum pH which is 5. It shows that at a concentration of 10 mg/l, the removal efficiencies gradually increase earliest at 12 minutes of reaction until 63% of removal efficiencies. The maximum removal efficiencies are 64%, and the removal took a maximum time of 45 minutes. Similar traits occurred for concentrations of 20 and 30 mg/l but the maximum removal efficiencies for each of them are nearly 61% and 59% respectively. It shows that at 10 mg/l concentration of Zn heavy metals, it shows a gradual increase of removal capabilities starting at 12 minutes until reaches the maximum removal efficiencies. With a significant quantity of H⁺ present at low pH, the surface of the PS might be protonated. Furthermore, the lower Cu2⁺ adsorption capability of PS is caused by H⁺'s ability to compete with Cu2⁺ for the same adsorption sites at low pH [10].



Figure 6: The effect of different adsorbent dosages on Zn heavy metals

Based on the Figure 6, the adsorbent dosage of 4% of EPS at concentration of 30 mg/l has the highest removal efficiencies of 56%. The lowest removal efficiencies is at concentration of 10 mg/l at 2% of dosage which is 11% of removal efficiencies. It can be observed from the above data, as the adsorbent dosage increase, the removal efficiencies increases as varying the concentration of Zn heavy metals. Adsorbent dose has a significant impact on adsorption capability. The larger the EPS dose, the greater the effectiveness of elimination. The maximum percentage of removal efficiencies is between 55% and 56%. There is an increase in the adsorption process if there is also particular contact time. 3% and 4% were still more higher of removal than 2% of EPS. Furthermore, as the amount of adsorber added grew, so did the removal efficiency [11].

4. Conclusion

The results significantly proved that the removal of Zn heavy metals has the maximum removal efficiency at pH values of 5 and adsorbent doses of 0.04 g. The findings indicate that the pH is the most important parameter with the largest influence on the percentage adsorption compared to the different dosages of adsorbers. The results effectively demonstrated that PS Cu NPs had strong binding site characteristics, allowing ion exchange with Zn ions. The active mass transfer between Cu NPs and Zn heavy metals generated considerable removal of Zn heavy metals, whereas PS acted as a trapping agent between the binding of Cu NPs and Zn. The polymers created in this work feature several internal pores and are easily cross-linked with various chemical groups, enabling them to selectively adsorb the intended pollutants. There are several uses in water treatment, most notably as an adsorbent for the removal and extraction of various heavy metals. According to the findings, EPS has the potential to be used as an adsorbent for Zn heavy metals in wastewater, yielding effective results, and is suitable for future study into its features.

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