Universal Journal of Green Chemistry
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Research Article

Removal of Heavy Metal Ions (Fe^{2+}, Mn^{2+}, Cu^{2+} and Zn^{2+}) on to Activated Carbon Prepared from Kashmiri Walnut Shell (*Juglans regia*)

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Received: 24 April 2024; **Revised:** 11 May 2024; **Accepted:** 13 May 2024

Abstract: Heavy metal pollution poses significant threats to the environment and human health, even at trace concentrations. In this study, activated carbon derived from Kashmiri walnut shell (Juglans regia) was investigated for its potential to adsorb heavy metal ions (Fe^{2+}, Mn^{2+}, Cu^{2+}, and Zn^{2+}). Standard solutions containing heavy metal ions at concentrations ranging from 10 to 50 ppm were prepared for adsorption experiments, i.e., at temperature 25 °C, and adsorbent dosage 1 g using a column mechanism. The activated carbon was first treated with 0.1M HCl and 0.5M ammonia solutions, and then washed with demineralised water. Subsequently, the metal ion solutions were passed through the column individually, and the filtrates were analyzed for heavy metal ion presence. The experimental results demonstrated that walnut shell-derived activated carbon exhibited promising adsorption capacity spanning from 0.36 mg/g for Zn^{2+}, 0.5 mg/g for both Mn^{2+} and Cu^{2+} and 0.54 mg/g for Fe^{2+} thus showing the adsorption trend as $Fe^{2+} > Mn^{2+} = Cu^{2+} > Zn^{2+}$. This study highlights the potential of using walnut shell-derived activated carbon as an effective and cost-efficient method for mitigating heavy metal pollution in contaminated water sources.

***Keywords*:** heavy metal; walnut shell; activated carbon; column; filtrate

1. Introduction

The escalation of heavy metal pollution in the environment can be predominantly attributed to the burgeoning human population and a plethora of anthropogenic activities. These activities encompass diverse sectors such as mining operations and the discharge of both treated and untreated waste effluents containing toxic metals and their derivatives from industries including tanneries, steel plants, battery manufacturing units, and thermal power plants [1,2]. Furthermore, the indiscriminate utilization of fertilizers and pesticides in agricultural practices exacerbates the degradation of water quality by amplifying heavy metal contamination, thereby engendering significant environmental and health concerns [3]. The deleterious effects of heavy metal toxicity extend to a spectrum of physiological and neurological impairments, including compromised mental and central nervous system functions, diminished energy levels, and damage to vital organs such as the lungs, kidneys, liver, and bloodstream [4].

Indeed, heavy metal contamination remains a pervasive challenge with far-reaching implications [5–8]. Chronic exposure to elevated levels of heavy metals poses a grave risk to human health, potentially precipitating a range of debilitating

DOI: https://doi.org/10.37256/ujgc.2120244806

conditions. Prolonged exposure to these toxic substances may instigate a gradual onset of physical, muscular, and neurological degenerative processes, reminiscent of neurodegenerative disorders like Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Moreover, there is an established correlation between chronic or repetitive long-term exposure to certain heavy metals and an increased susceptibility to cancer [9].

Given the alarming implications associated with heavy metal contamination of water sources, it is imperative to devise robust strategies to mitigate these risks and safeguard both environmental integrity and public health. Addressing the removal of heavy metals from drinking water emerges as a pressing priority to mitigate adverse outcomes. In this context, the utilization of materials such as activated carbon derived from plant by-products presents a promising avenue for intervention [10].

The efficacy of activated carbon as an adsorbent material is universally recognized, particularly for its capacity to sequester, eliminate, or reduce the concentration of various dissolved pollutants in water, including both organic and inorganic compounds [11]. Its high porosity and extensive surface area facilitate a substantial volume of contaminant absorption, while the functional groups on its surface, such as carboxyl and phenols, enable effective chemical bonding with contaminants, thereby enhancing its adsorption capabilities [11,12]. However, the application of activated carbon is not devoid of challenges. The costs associated with its production and regeneration can be prohibitive, affecting its widespread use [13]. Additionally, the adsorption sites may become saturated over time, which diminishes the carbon's effectiveness and necessitates its replacement or regeneration [14]. The adsorption process is also selective, which means it may not be equally effective against all pollutants, potentially requiring additional treatment methods for certain contaminants [12]. Despite these limitations, the advantages of activated carbon, such as its porosity, surface area, and functional groups render it an indispensable adsorbent in water treatment systems [13–16]. A balanced approach is essential to leverage its benefits while addressing its disadvantages.

In the context of escalating environmental concerns over heavy metal contamination in water bodies, the current study pivots on a critical evaluation of activated carbon derived from walnut shells as an adsorbent. This research aims to elucidate the capacity of this bio-based activated carbon to effectively remove heavy metals from aqueous solutions. The choice of walnut shells as a precursor for activated carbon production is underpinned by their inherent properties, such as high carbon content and a substantial amount of lignin, which upon activation, yield a material with a high surface area and porosity [17].

The state of the art in this domain indicates that activated carbon from walnut shells exhibits a remarkable affinity for heavy metals, owing to its surface chemistry and pore structure, which are conducive to the adsorption process [18]. Studies have demonstrated the potential of this material in capturing heavy metals like chromium (Cr), lead (Pb), and cadmium (Cd) from contaminated water [19]. The activation process typically involves chemical agents like potassium hydroxide (KOH) or sodium hydroxide (NaOH), which enhance the adsorptive properties of the resulting carbon [20].

Recent advancements have focused on optimizing the activation process to maximize the adsorption efficacy of walnut shell-derived activated carbon. Innovations in this field include the application of response surface methodology to determine the optimal conditions for heavy metal removal, thereby improving the efficiency and cost-effectiveness of the process. Furthermore, computational calculations and non-covalent interaction (NCI) analyses have provided deeper insights into the adsorption mechanisms at the molecular level [17].

Despite the promising results, challenges such as the regeneration of spent activated carbon and the selective adsorption of specific heavy metals remain. Future research directions involve enhancing the selectivity and capacity of activated carbon, as well as developing sustainable and economically viable regeneration techniques [18]. The main objective of this study is to develop cost effective walnut shell -derived activated carbon from the locally available sources for the removal of heavy metal contaminants from the polluted water. The ongoing research in this field continues to refine the adsorption processes, aiming to achieve higher efficiencies and broader applications in water treatment.

2. Material and Methods

The walnut shells were procured from the local market.

2.1 *Materials*

The following materials and reagents were utilized in the current study:

Ferric Chloride ($FeCl_3$) Anhydrous: Sourced as an analytical reagent (AR), this compound has a molecular weight of 162.21 g/mol and a purity of 96%.

Zinc Chloride ($ZnCl_2$): Also procured as an analytical reagent (AR), zinc chloride has a molecular weight of 136.28 g/mol with a purity exceeding 95%.

Copper (II) Chloride Dihydrate ($CuCl_2 \cdot 2H_2O$): With a molecular weight of 170.48 g/mol and a high purity of 99%.

Manganese Sulphate Monohydrate ($MnSO_4 \cdot H_2O$): This compound, used as an analytical reagent (AR), has a molecular weight of 169.06 g/mol and a purity of 99%.

Each reagent was selected based on its purity and specific role in the experimental procedures, ensuring the reliability and reproducibility of the study's results.

2.2 *Preparation of Adsorbent Material (Activated Carbon)*

The activated carbon was prepared using walnut shell raw material, which was procured from a local market. The raw shells were first oven-dried at a temperature maintained between 140–160 °C for duration of 2–3 h to ensure the removal of all moisture content[21]. Subsequently, the dried shells were ground and sieved through a sieve shaker to achieve a uniform particle size suitable for activation. Some of the physical properties of activated carbon such as texture, bulk density (Equation (1)), particle density (Equation (2)) and percentage porosity (Equation (3)) were done as per the technique described earlier[20]. The texture was qualitatively assessed by the touch-and-feel method, allowing the categorization of the samples into the appropriate texture class.

$$\text{Bulk density (g/mL)} = (W2 - W1)/V \tag{1}$$

Where:
W1 is the weight of an empty bottle,
W2 is the weight of bottle and charcoal,
V is the volume (mL) of water needed to fill the bottle

$$\text{Particle density(g/mL)} = W/((W3 - W) - W4) \tag{2}$$

Where:
W is the weight of sample taken,
W3 is the weight of bottle and water,
W4 is the weight of bottle, sample and water

$$\text{Percentage porosity} = 100 - (\text{Bulk density})/(\text{Particle density}) \times 100 \tag{3}$$

2.3 *Preparation of An Adsorbent Packed Column*

The charred adsorbent material packed in separate glass columns (600 mm length, 40 mm diameter) with sintered disc and stopcock. The column was packed with 1g of the adsorbent. The material was washed twice with demineralised water before use.

2.4 *Adsorption Experiments*

Experimental Procedure for Adsorption of Heavy Metals:

Preparation of Standard Solutions: Solutions of heavy metals, specifically iron (Fe^{2+}), manganese (Mn^{2+}), copper (Cu^{2+}), and zinc (Zn^{2+}), were prepared at five different concentrations: 10, 20, 30, 40, and 50 parts per million (ppm).

Column Preparation: An activated carbon column was prepared by adding 1 gram of the adsorbent. The column was then conditioned following a two-step washing protocol: initially with 0.1M hydrochloric acid (HCl) and subsequently with 0.5M ammonia solution. This procedure aligns with the established protocol referenced in[22]. After the chemical treatments, the column was thoroughly rinsed with de-mineralized water to eliminate any remaining reactive substances.

Adsorption Process: In the adsorption experiments, 20 mL aliquots of metal ion solutions (Fe^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}) at varying concentrations were processed through an activated carbon column. The pH was adjusted to 5.0 for optimal adsorption of Zn^{2+} and Cu^{2+} ions, and to 6.0 for Fe^{2+} and Mn^{2+} ions. A consistent contact time of 90 min and a flow rate of 10 mL/min were maintained across all trials.

Post-Adsorption Analysis: Following the adsorption, the filtrates were collected from each experiment. These samples were then analyzed to determine the concentration of heavy metal ions remaining, thereby quantifying the adsorption capacity of the activated carbon.

The methodology followed for the study is depicted in the Figure 1.

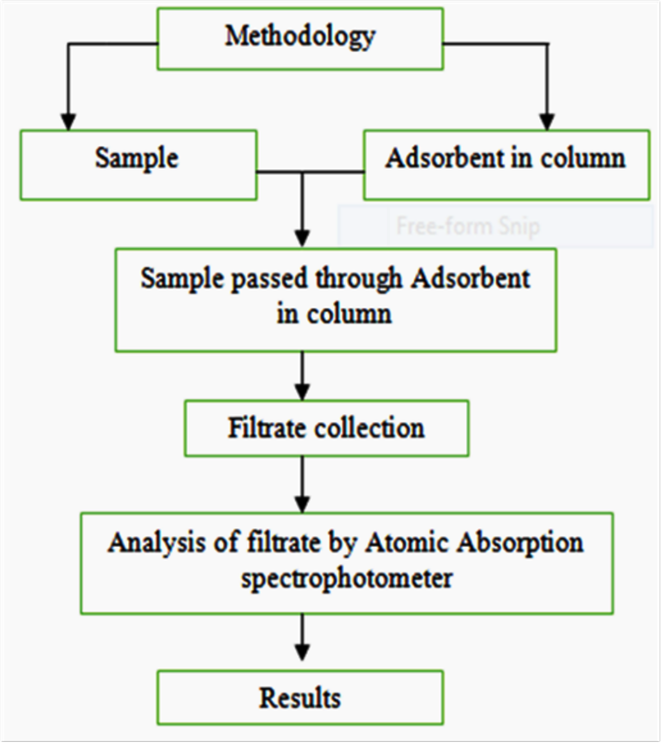

Figure 1. Research Methodology.

2.5 *Analysis and Calculations*

The filtrates obtained after each treatment were subjected to atomic absorption spectrophotometer analysis (AAS) for presence of heavy metal ions. Atomic Absorption Spectroscopy (AAS) (WFX-210, Rayleigh, BRAIC,

Beijing, China) was used to determine the concentration of the metal ions. A mixture of compressed air as oxidant and acetylene as fuel were employed. The measurement of each metal was carried out with the help of standard calibration curve at their respective wave lengths.

After the filtrates were analysed under AAS, calculations were made using (Equations (4) and (5)).

$$\text{Adsorption Capacity (mg/g)} = \frac{(C0 - Cf) \times V}{W} \tag{4}$$

$$\text{Percent Adsorption } = \frac{(C0 - Cf) \times 100}{C0} \tag{5}$$

Where:
C_0 is initial concentration in ppm,
C_f is final unabsorbed concentration in ppm.
V is the volume in liters.
W is the dry weight of adsorbent in grams.

3. Results and Discussion

The investigation delved into the adsorption behaviour of heavy metals using 1 g of activated carbon across a spectrum of concentrations, ranging from 10 ppm to 50 ppm. The results revealed intriguing insights into the adsorption capacities and percentages for various heavy metals. Firstly, focusing on the adsorption of Fe^{2+} onto walnut shell activated carbon, the findings exhibited a considerable range in adsorption capacity, spanning from 0.2 mg/g to 0.54 mg/g. This variation suggests the affinity of the activated carbon for Fe^{2+} ions across different concentrations. Additionally, the corresponding adsorption percentage ranged between 100% and 54%, indicating the effectiveness of the adsorbent in removing Fe^{2+} ions from the aqueous phase. These observations are visually represented in Figures 2 and 3, respectively. Similarly, the adsorption behaviour of Mn^{2+} onto the activated carbon displayed notable variability in adsorption capacity, ranging from 0.2 mg/g to 0.5 mg/g. This indicates the ability of the adsorbent to capture Mn^{2+} ions from solutions with differing concentrations. Correspondingly, the adsorption percentage ranged from 100% to 50%, as shown in Figures 4 and 5, reflecting the efficacy of the adsorption process across the concentration gradient. Moreover, the investigation examined the adsorption capacity of Cu^{2+} onto the prepared adsorbent, revealing a range of 0.2 mg/g to 0.5 mg/g. This underscores the adsorbent's capability to capture Cu^{2+} ions across varying concentrations. The associated adsorption percentage ranged between 100% and 50%, as illustrated in Figures 6 and 7, indicating the effectiveness of the adsorbent in removing Cu^{2+} ions from solution. Furthermore, the adsorption of Zn^{2+} onto walnut shell charcoal was investigated, revealing an adsorption capacity spanning from 0.2 mg/g to 0.36 mg/g. This range signifies the adsorbent's ability to capture Zn^{2+} ions across different concentrations. The adsorption percentage fluctuated between 36% and 100%, as presented in Figures 8 and 9, highlighting the varying efficacy of the adsorption process at different Zinc concentrations.

Overall, the adsorption potential of walnut shell activated carbon for heavy metals followed the order: $Fe^{2+} > Mn^{2+} = Cu^{2+} > Zn^{2+}$. This sequence indicates the relative affinities of the adsorbent for different heavy metal ions and provides valuable insights into its efficacy in removing these contaminants from aqueous solutions.

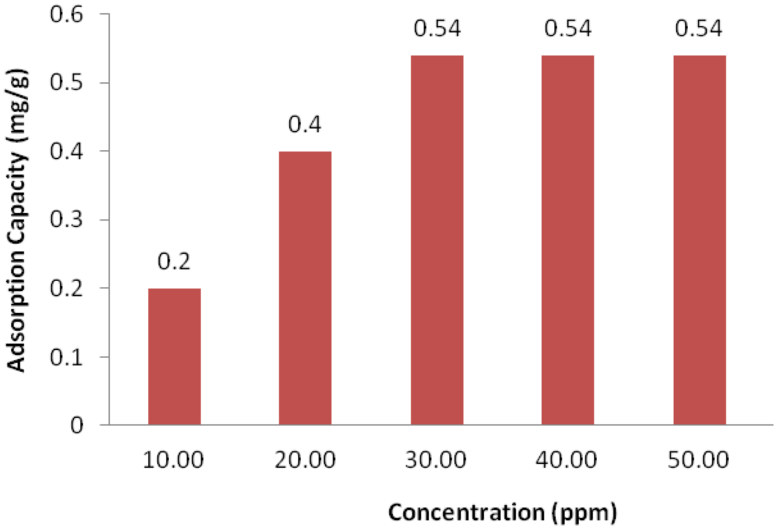

Figure 2. Adsorption capacity of walnut shell carbon for Fe^{2+}.

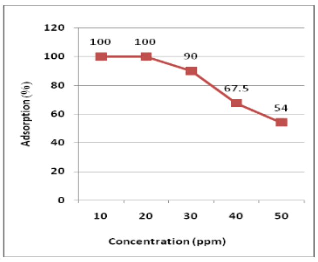

Figure 3. Percentage removal of Fe^{2+} by walnut shell carbon.

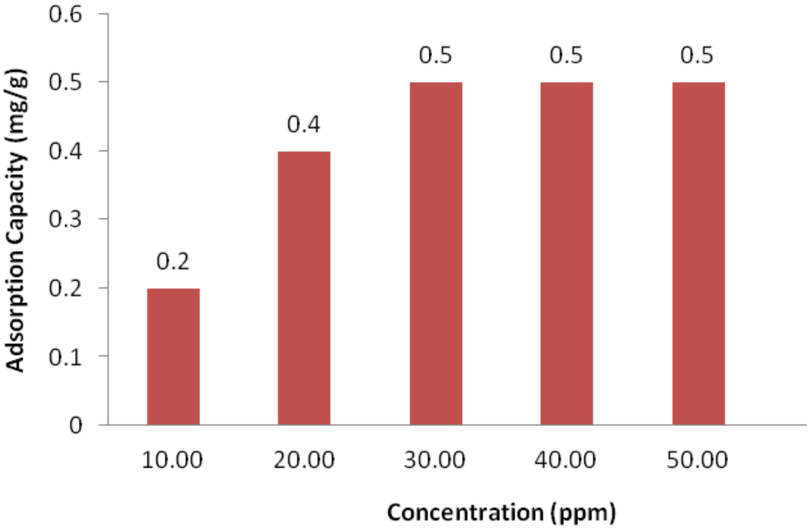

Figure 4. Adsorption capacity of walnut shell carbon for Mn^{2+}.

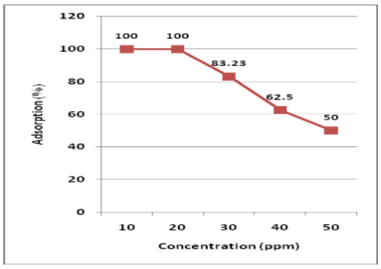

Figure 5. Percentage removal of Mn^{2+} by walnut shell carbon.

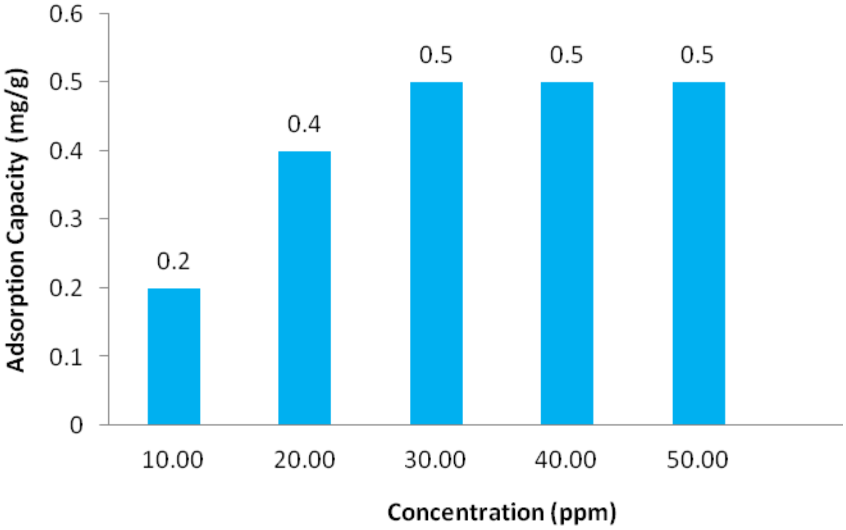

Figure 6. Adsorption capacity of walnut shell carbon for Cu^{2+}.

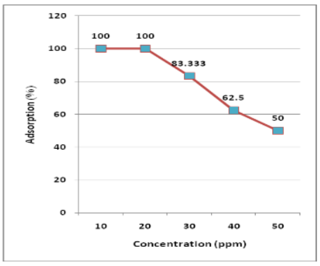

Figure 7. Percentage removal of Cu^{2+} by walnut shell carbon.

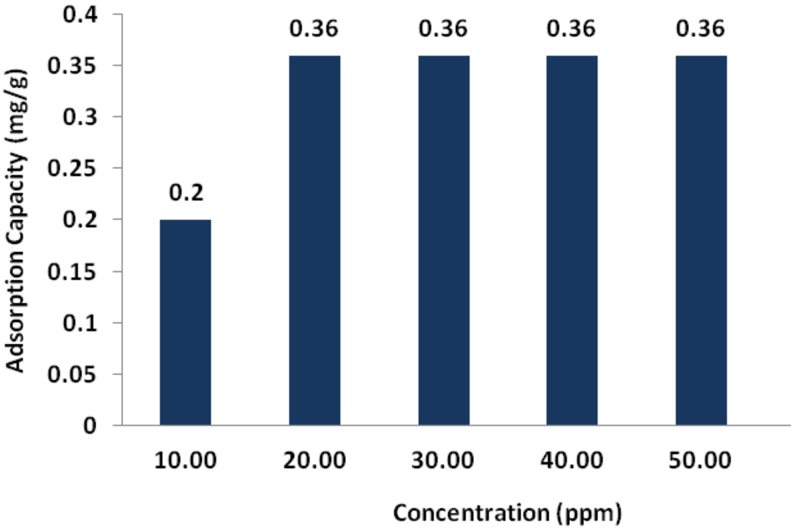

Figure 8. Adsorption capacity of walnut shell carbon for Zn^{2+}.

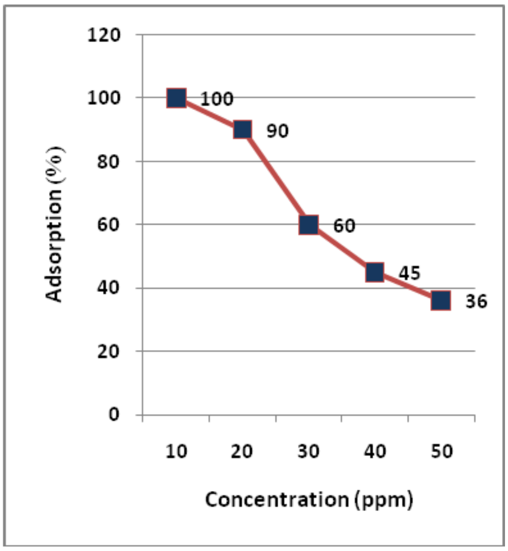

Figure 9. Percentage removal of Zn^{2+} by walnut shell.

The decrease in adsorption efficiency with increasing metal ion concentration, observed from 10 ppm to 50 ppm, highlights important insights into the chemical behavior of the adsorbent. At lower metal ion concentrations, the adsorbent possesses an abundance of negative surface sites, allowing it to effectively attract and accommodate the relatively small number of positively charged metal ions present in the water. Consequently, this facilitates the near-complete removal of metals from the water, achieving 100% removal efficiency at the lower metal ion concentration because of the enough adsorption sites available on the adsorbent.

However, as the concentration of metal ions in the water increases, the number of available metal ions surpasses the capacity of the adsorbent's negative surface sites. This leads to overcrowding of the negative charged sites on the adsorbent's surface, thereby reducing the availability of binding sites for the increased population of metal ions. Consequently, the adsorbent fails to provide sufficient space for binding the higher concentration of metal ions, resulting in a decrease in adsorption capacity.

This decrease in adsorption efficiency at higher metal ion concentrations underscores the importance of considering the chemical behavior of the adsorbent in relation to the concentration of metal ions in the water. Additionally, it emphasizes the necessity of optimizing adsorption conditions to maximize removal efficiency, particularly in scenarios with elevated metal ion concentrations.

The physical properties of walnut shell carbon, as detailed in Table 1, provide further context for understanding its adsorption behavior and underscore the importance of characterizing the adsorbent material to optimize its performance in heavy metal removal applications.

Table 1. Physical properties of walnut.

Texture	Bulk Density (g/mL)	Particle Density (g/mL)	Percentage Porosity (%)
Loamy	0.06	1.03	94.17

4. Conclusions

Adsorption of Fe^{2+} on walnut shell charcoal revealed that adsorption capacity of walnut shell charcoal varied from 0.2 mg/g to 0.54 mg/g with maximum adsorption capacity of walnut shell charcoal for Fe^{2+} found to be 0.54 mg/g. Further, adsorption of Fe^{2+} on walnut shell charcoal was found in the range of 54 to 100%. Maximum adsorption capacity for Mn^{2+} of walnut shell charcoal was found to be 0.5 mg/g with adsorption capacity varying from 0.2 mg/g to 0.5 mg/g. The adsorption of Mn^{2+} on walnut shell charcoal was in the range of 50 to 100%. Studies on the adsorption of Cu^{2+} on walnut shell charcoal revealed that adsorption capacity of walnut shell charcoal varied from 0.2 mg/g to 0.5 mg/g with the maximum adsorption capacity of walnut shell charcoal for Cu^{2+} of 0.5 mg/g. The adsorption of Cu^{2+} was found in the range of 50 to 100%, as was seen in the case of Mn^{2+}. Adsorption of Zn^{2+} on walnut shell charcoal revealed that adsorption capacity of walnut shell charcoal varied from 0.2 mg/g up to a maximum of 0.36 mg/g. The adsorption of Zn^{2+} was observed to be in the range of percent found in range of 36 to 100% with walnut shell charcoal. The experimental findings revealed that activated carbon prepared from the wall nut shell showed effective adsorption ability for the removal of heavy metal ions from their aqueous phase. Furthermore, since walnut shells are inexpensive and locally available as such this study provides cost effective means for removal of heavy metal ions from contaminated water.

Author Contributions

Suhail Abdullah Malik designed and conducted experiments, prepared activated carbon, and analyzed data. Sharief-ud-din Khan supervised the project and contributed to its conception. Bashir Ahmad Dar led the writing and data interpretation, coordinated the research, and handled manuscript submissions.

Acknowledgments

The authors thank all those who assisted with this work and appreciate the insightful suggestions provided by the peer reviewers.

Conflict of interest

There are no conflict of interest associated with this study.

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