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Removal of Heavy Metal Ion (Fe2+, Mn2+, Cu2+ and Zn2+) on to Activated Carbon prepared from Kashmiri Walnut Shell (Juglans regia)

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Abstract
Heavy metal pollution has a severe repercussion on environment. Their occurrence in the body even in the trace concentrations results in neurological, behavioural and physiological problems. In the present study activated carbon was prepared out of Kashmiri walnut shell (Juglans regia) for assessing its adsorption removal capacity by treatment on to the standard solutions of heavy metal ions (Fe2+, Mn2+, Cu2+and Zn2+). For the adsorption experiments, standard solutions of 10, 20, 30, 40 and 50 ppm of the heavy metals were prepared. Column adsorption mechanism was done for the study process. The column having 1g of the absorbent was first washed with 0.1M HCl and 0.5M ammonia solutions. The column was finally washed with demineralised water. Then, 20 ml of different standard metal ion solutions (10-50 ppm) were passed through the column, separately. The filtrates were collected and analysed for the presence of heavy metal ions. The experimental finding revealed that activated carbon prepared out of walnut shell showed promising adsorption ability for the removal of heavy metals from aqueous phase. Adsorbing behaviour of activated carbon prepared, showed the trend of Fe2+> Mn2+ = Cu2+> Zn2+.
Key Words: Heavy metal, Walnut Shell, Activated carbon, Column, Filtrate.

1. Introduction

Heavy metal pollution in the environment is attributed to expanding human population, anthropogenic activities like mining, disposal of treated and untreated waste effluents containing toxic metals as well as their compounds from different industries such as tannery, steel plants, battery industries and thermal power plants [1, 2]. Indiscriminate use of fertilizers and pesticides in agriculture also deteriorate water quality by enhancing heavy metal contamination, rendering severe environmental and health problems. Heavy metal toxicity could result from contaminated drinking water or their flow through food chain [3].Heavy metal contamination hazards still remain a problem at large effect [4,5,6,7]. Heavy metal toxicity can result in damaged or reduced mental and central nervous functions, lower energy levels and damage to blood consumption, lungs, kidneys, liver and other vital organs. Long term exposure may result in slowly progressing physical, muscular and neurological degenerative processes that mimic Alzheimer's disease, Parkinsons disease, muscular dystrophy and multiple sclerosis. Chronic or repeated long-term exposure to some metals may cause cancer [8]. In view of the facts associated with heavy metal contamination of water and its significant effect on in health. Therefore, the remedial measures could play more significant role to minimize the level of contamination and risks to human health. Thus, to maintain the environmental quality and avoid health hazards, it is necessary to remove the heavy metals from drinking water. Materials such as activated carbon from plant by-products have shown their potential effectiveness [9].

Adsorption potential of activated carbon has been widely acknowledged as an effective technique of separation, elimination or lowering the concentration of a wide range of dissolved pollutants including organic and inorganic components in water [10]. Activated carbons out of their porosity, large surface area, presence of surface functional groups makes them as effective adsorbent material [11, 12, 13, 14]. The objective of the present study was to assess the adsorption ability of activated carbon prepared out of walnut shell for removal of heavy metals from aqueous phase.

2.Material and Methods

The walnut shells were procured from the local market.

2.1 Standard solutions of the metal adsorbates used in the present research work were prepared from the following chemicals:

2.1.1 Ferric chloride (FeCl3 anhydrous) analytical reagent (AR), molecular weight 162.21, purity 96 %.

2.1.2Zinc chloride (ZnCl2) AR, molecular weight

136.28, purity >95%.
2.1.3 Copper (II) chloride dihydrate ($CuCl_2.2H_2O$) AR, molecular weight 170.48,purity 99%.
2.1.4 Manganese sulphate monohydrate ($MnSO_4.H_2O$) AR, molecular weight 169.06,purity 99%.

2.2Preparation of adsorbent material (activated carbon)

For the purpose walnut shell raw material obtained from the local market raw oven dried [15].Temperature of the oven was maintained at 140-160 °C for period of about 2-3 hr.It was grinded than and sieved through sieve shaker. Some of the physical properties of activated carbon such as texture, bulk density, particle density and percentage porosity were done as per the technique described by [16].

Texture of samples was determined by touch and feeling by finger method and proper texture class was considered.

$$\text{Bulk density (g/ml)} = \frac{W2 - W1}{V}$$

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

$$\text{Particle Density (g/ml)} = \frac{W}{(W2\text{-}W) - W3}$$

Where:
W is the weight of sample taken.
W_2 is weight of bottle and water.
W_3 is the weight of bottle, sample and water.

$$\text{Percent porosity} = 100 - \frac{\text{Bulk density}}{\text{Particle Density}} \times 100$$

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 Adsorbing Experiments

For the adsorption experiments, standard solutions of 10, 20, 30, 40 and 50 ppm of the heavy metals (Fe^{2+}, Mn^{2+}, Cu^{2+} and Zn^{2+}) were prepared. The column having 1g of the absorbent was first washed with 0.1M HCl and 0.5M ammonia solutions, subsequently [17]. The column was finally washed with demineralised water. Then, 20 ml of different standard metal ion solutions (10-50 ppm) were passed through the column, separately. The filtrates were collected and analysedfor the presence of heavy metal ions. The methodology followed for the study is depicted in the Fig 1.

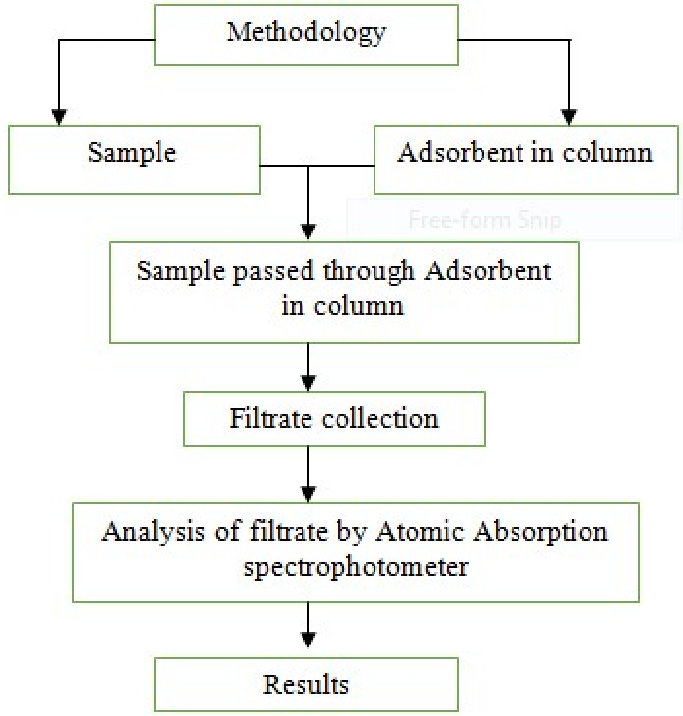


Fig 1. Research Methodology

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. 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 like

Cu^{2+} (λ_{max}=324.7 nm).
Fe^{2+} (λ_{max}=248.3 nm).
Mn^{2+} (λ_{max}= 279.59 nm).
Zn^{2+} (λ_{max} =213.9 nm).After the filtrates were analysed under AAS following calculations were made.

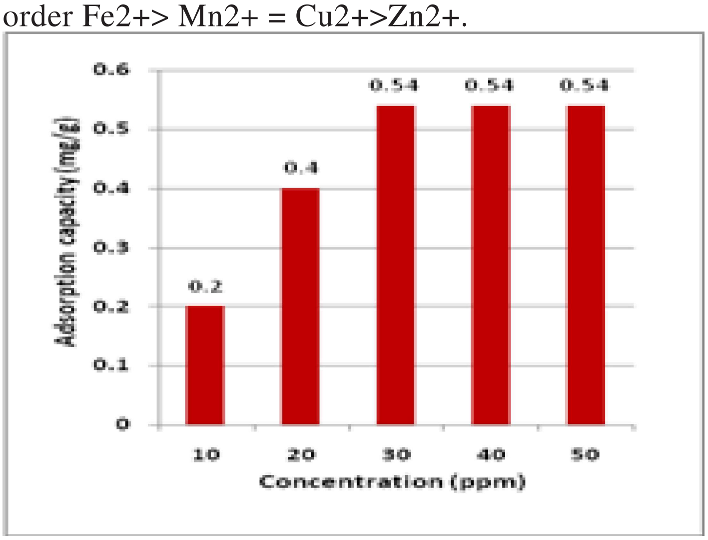
$$\text{Adsorption capacity (mg/g)} = \frac{(C0 - Cf) \times V}{W}$$

$$\text{Adsorption percent} = \frac{(C0 - Cf) \times 100}{C0}$$

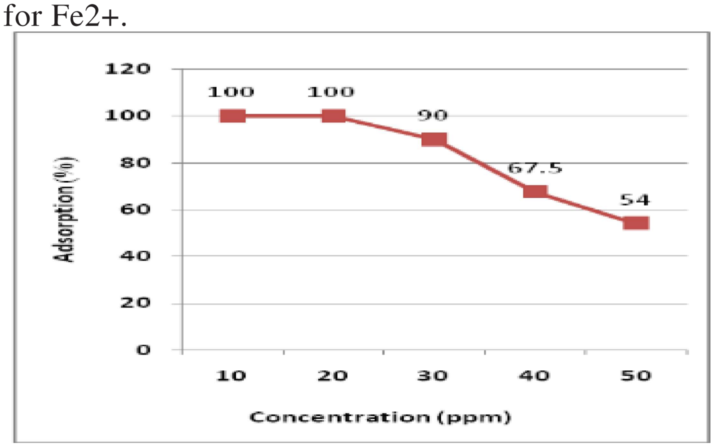
Where:
C0 is initial concentration in ppm,
Cf is final unabsorbed concentration in ppm.
V is the volume in liters.
W is the dry weight of adsorbent in grams.

3.Results and Discussion

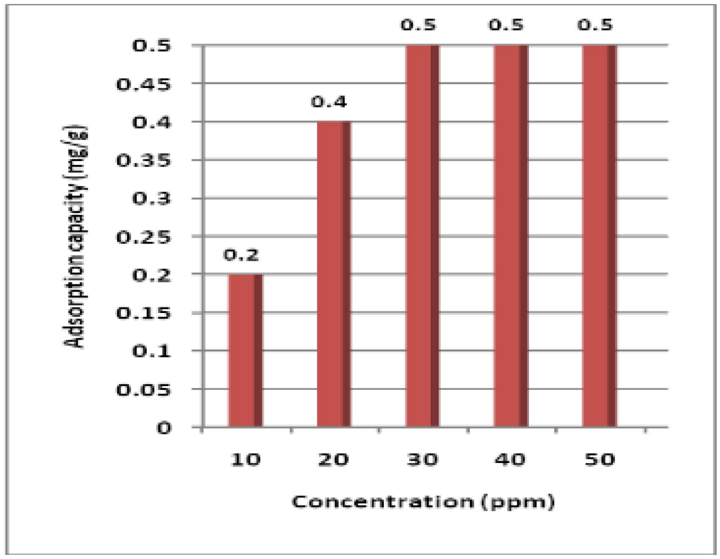
Adsorption behaviour was studied on 1g of activated carbon with the varying concentration of heavy metals from 10ppm to 50ppm.Adsorption of Fe2+ on walnut shell activated carbon showed the results of adsorption capacity in a range of 0.2mg/g to 0.54 mg/g (Graph 1)andadsorption percent was found to be in the range of 100 and 54% (Graph.2).Adsorption behaviourof Mn2+ on to the activated carbon depicted the adsorptioncapacity ranged between 0.2 mg/gto 0.5mg/g (Graph.3) and the adsorption percent in the range of 100 and 50 % (Graph.4).For Cu2+ adsorbent prepared exhibited the adsorption capacity in a range of 0.2 mg/g to 0.5mg/g(Graph.5.) and the adsorption percent ranged between 100 and 50 % (Graph.6.).Adsorption of Zn on walnut shell charcoal is depicted in (Graph.7 and 8.). The data of adsorption capacity of walnut shell charcoal appeared in the range of 0.2 mg/g to 0.36 mg/g and adsorption percent ranged between 36 and 100 %.Adsorbing potential of walnut shell activated carbon for heavy metals followed the order Fe2+> Mn2+ = Cu2+>Zn2+.



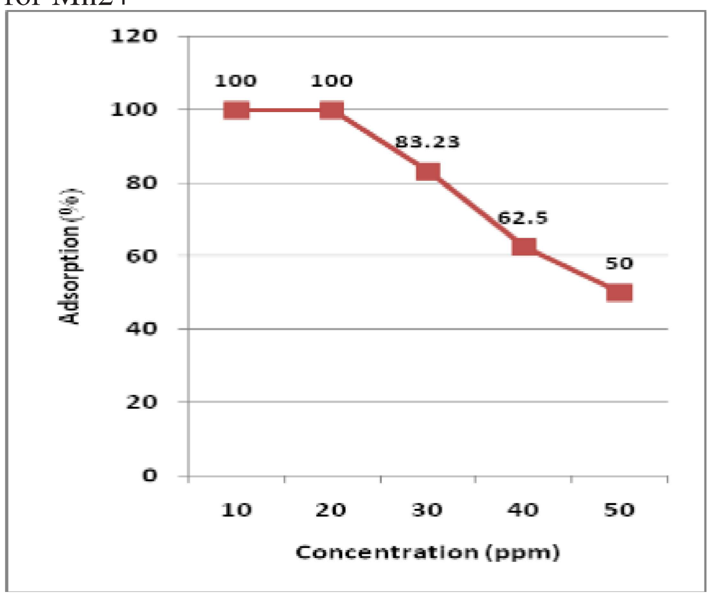
Graph 1Adsorption capacity of walnut shell carbon for Fe2+.



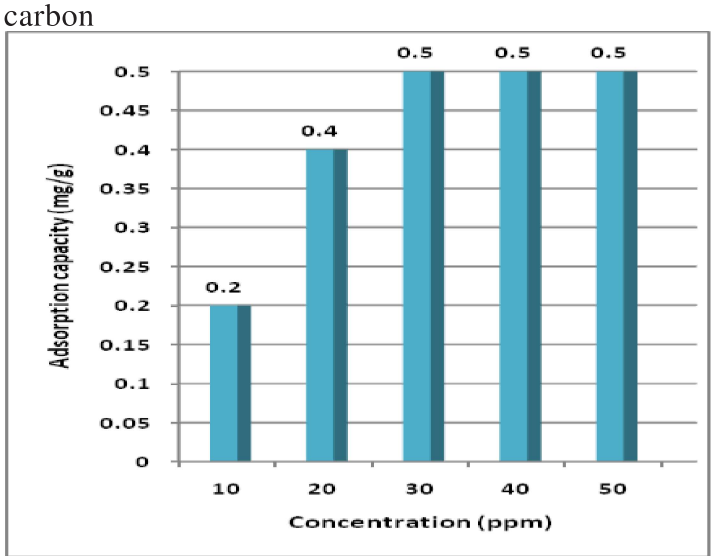
Graph.2. Percentage removal of Fe2+ by walnut shell carbon.



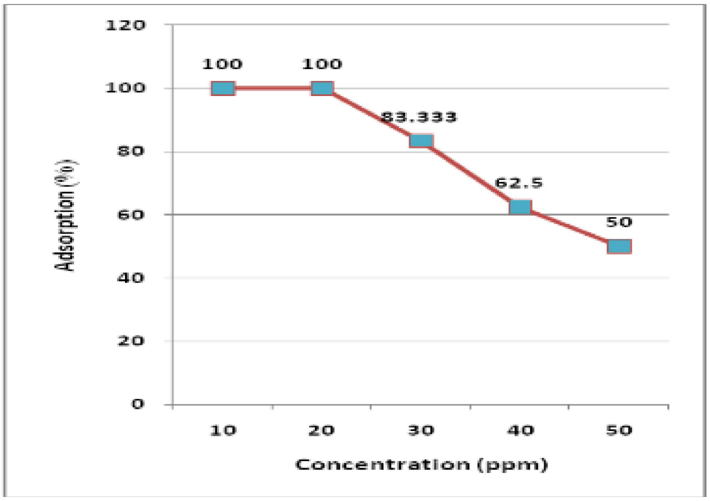
Graph.3.Adsorption capacity of walnut shell carbon for Mn2+



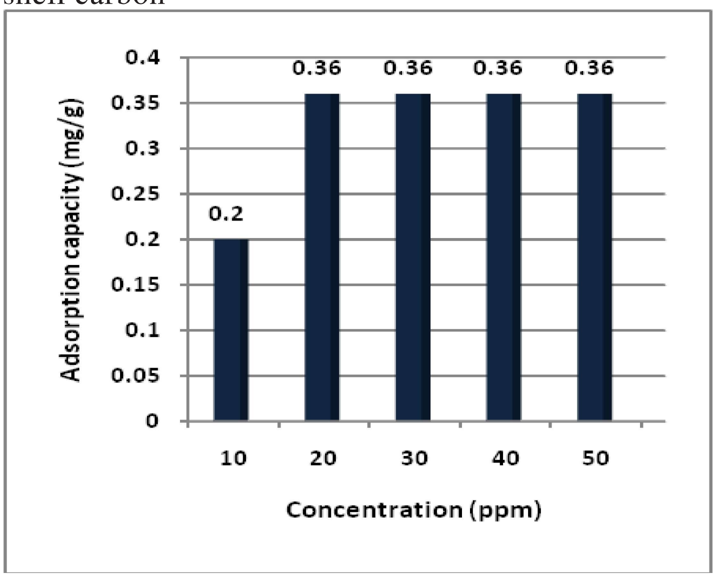
Graph.4. Percentage removal of Mn2+by walnutshell carbon



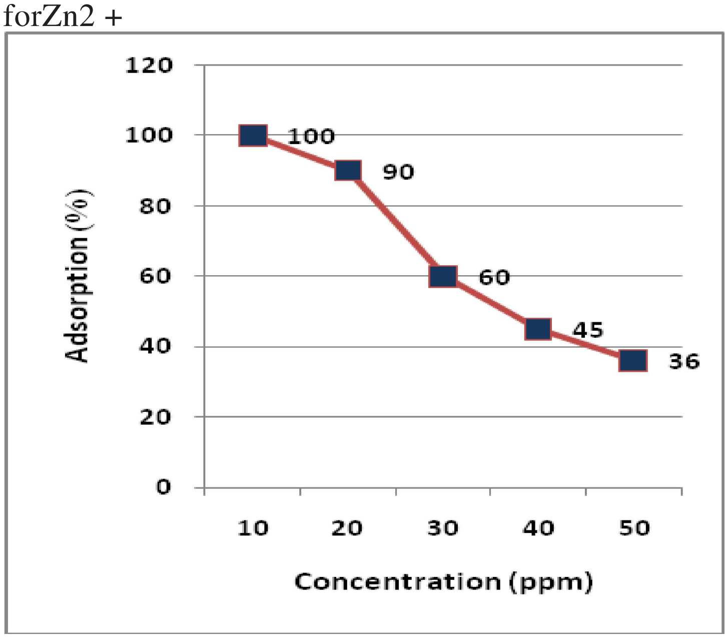
Graph.5. Adsorption capacity of walnut shell carbon for Cu2+



Graph.6. Percentage removal of Cu2+ by walnut shell carbon



Graph.7. Adsorption capacity of walnut shell carbon forZn2 +



Graph.8.Percentage removal of Zn2+ by walnut shell

Adsorption behavioural pattern kept on declining as the concentration of metal ions was enhanced from 10ppm to 50ppm. This obviously suggests the chemical behaviour of the adsorbent that at the lower population of the metal ions in water the adsorbent had more than enough negative surface to attract and accommodate the less number of available positively charged metal ions, that in turn, affecting 100% removal of metals from water. As soon as ionic concentration of metals increases or the adsorbent came into contact with higher population of adsorbate ions, the negative charged sites at the surface becomes overcrowded. Therefore, the adsorbent failed to provide adequate space of binding to the increased population of metal ions. This apparently causes lesser removal capacity of the adsorbent at exceedingly high levels of metals presence in water. The physical properties of walnut shell carbon worked out were as in table1.

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. Conclusion

Adsorption of Fe 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 found to be 0.54 mg/g. Further, adsorption of Fe on walnut shell charcoal was found in the range of 54 to 100 %.

Maximum adsorption capacity for Mn2+ 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 Mn2+ on walnut shell charcoal was in the range of 50 to 100 %.

Studies on the adsorption of Cu 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 of 0.5 mg/g. The adsorption of Cu was found in the range of 50 to 100%, as was seen in the case of Mn2+.

Adsorption of Zn 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 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 preparedfrom 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 heavymetal ions from contaminated water.

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