

RESEARCH ARTICLE | AUGUST 05 2021

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AIP Conference Proceedings 2352, 040012 (2021)

<https://doi.org/10.1063/5.0053480>



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The Mechanistic Route for the Removal of Heavy Metals Ions from Water on Nanoparticle Incorporated Biochar

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Abstract. In the modern world, the water pollution becomes the biggest challenge worldwide. The heavy metals contaminated water is of great concern, due to its non-biodegradable nature and it can bioaccumulate in the food web which caused serious health risk to human beings such as cancer, damage of kidney, liver and CNS. Therefore, it is an urgent need to eliminate heavy metals from the water. Several remediation methods which are employed such as ion exchange, electro dialysis, chemical precipitation, adsorption and flotation. Amongst them biosorption is the best method for the removal of heavy metals due to its lower cost and environmentally friendly nature. The efficiency of the biochar can be enhanced by the loading the metal nanoparticle on the surface of biochar. The heavy metals ions adsorbed on the surface of the biochar by different mechanism reduction, surface complexation, co-precipitation, ion exchange and electrostatic interaction.

Keyword: Heavy Metals; Adsorption; Biochar; Nanoparticle

INTRODUCTION

Nowadays, heavy metals pollution has become a big concern globally which adversely influenced the health of human owing to their non-biodegradable nature and bioaccumulation through food chain [1]. They are added into the water by anthropogenic activities like smelting and mining, production of electric appliances, utilization of pesticides in agriculture, paper industry, electroplating, which are responsible for the increasing level into the surface water as well as ground water, as a result the quality of water decline as shown in Figure 1 [2].

Conventionally various remediation methods have been employed for the elimination of heavy metals from the water, such as chemical precipitation, ion exchange, membrane filtration, electro dialysis and flotation as shown in Figure 2 [3-4]. Out of which biosorption is best because it is an economical and feasible method for the remediation of heavy metals from the water [5-1]. Bioadsorbents are the cheap, found abundantly and environment friendly, amongst them biochar emerging as the most utilised and effective bioadsorbent. Currently environmental researcher attracted toward the application of biochar in remediation of heavy metals ions from aqueous solution. It is believed that it may be the one of the best alternative adsorbent than other bioadsorbent for remediation of heavy metals from the water [6]. It is a carbon-rich, finely ground porous, product of thermal degradation obtained by slow of fact pyrolysis of biomass in oxygen-limiting atmosphere [7].

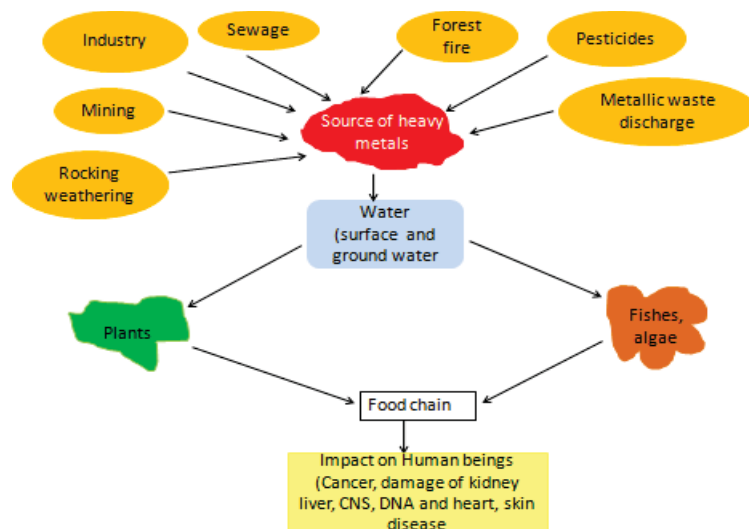


FIGURE 1. Representation of sources of heavy metals in water and their adverse effects on the human beings

Owing to their unique characteristics including generation of bioenergy, soil fertility and carbon sequestration potential biochar has drawn higher attention [8]. The large surface area, higher porosity and carbon-rich of biochar are the most significant characteristics in the adsorption of heavy metals from the polluted water [9]. In addition to this, presence of functional groups, for example phenolic, hydroxyl, amino, carboxyl groups and alkyl on the biochar surface has a greater affinity to adsorb metals from polluted water like mercury (Hg), nickel (Ni), zinc (Zn), chromium (Cr), lead (Pb), , manganese (Mn) copper (Cu) and cadmium (Cd) [10]. Different type of biowaste has been employed for the generation of biochar, such as agro waste, industrial waste and diary waste [11-13].

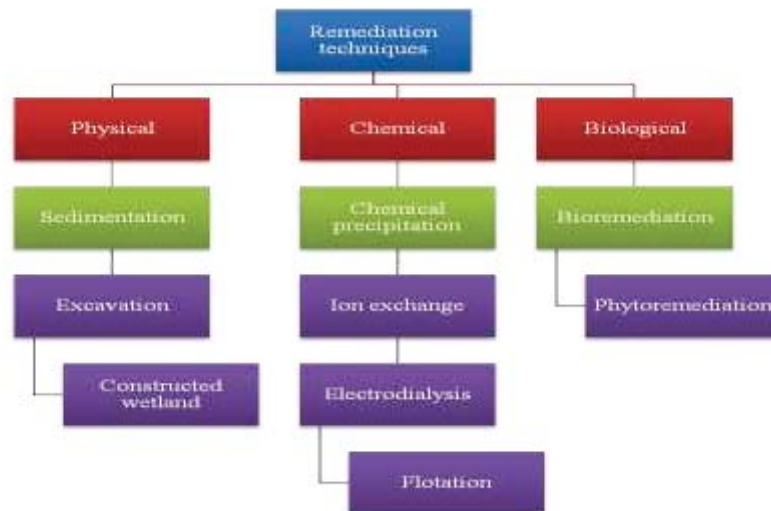


FIGURE 2. Remediation techniques for heavy metals present in water

MECHANISTIC ROUTE FOR ADSORPTION OF HEAVY METALS ON NANOSCALE METAL LOADED BIOCHAR

The nano scale metals loaded biochar has been utilised for the removal of heavy metals from the water [14]. As the nano material effectively loaded into the pores of biochar or on the surface of biochar which results in considerably change in chemical as well as physical properties including shift of surface functional groups, alteration in surface

charge and formation of graphite shape. In addition to these, they may also supply co-precipitation precursor, high electron transferring medium and higher reduction reactivity. Therefore, mechanism involving in remediation of heavy metals ions from the water are very complexed. Furthermore, the different properties of heavy metals ions for example redox potential, electronegative, hydrated ionic radius and valence state might be significantly impact the interaction behaviour between the heavy metals and biochars. Therefore, its necessary to recognised mechanism involved in the adsorption of heavy metals ions from the water on nanoscale metals loaded biochar to increase the viability of application of nanoscale metals loaded biochar in remediation of heavy metal ions. The probable mechanism account in the literature is depicted in Figure 3.

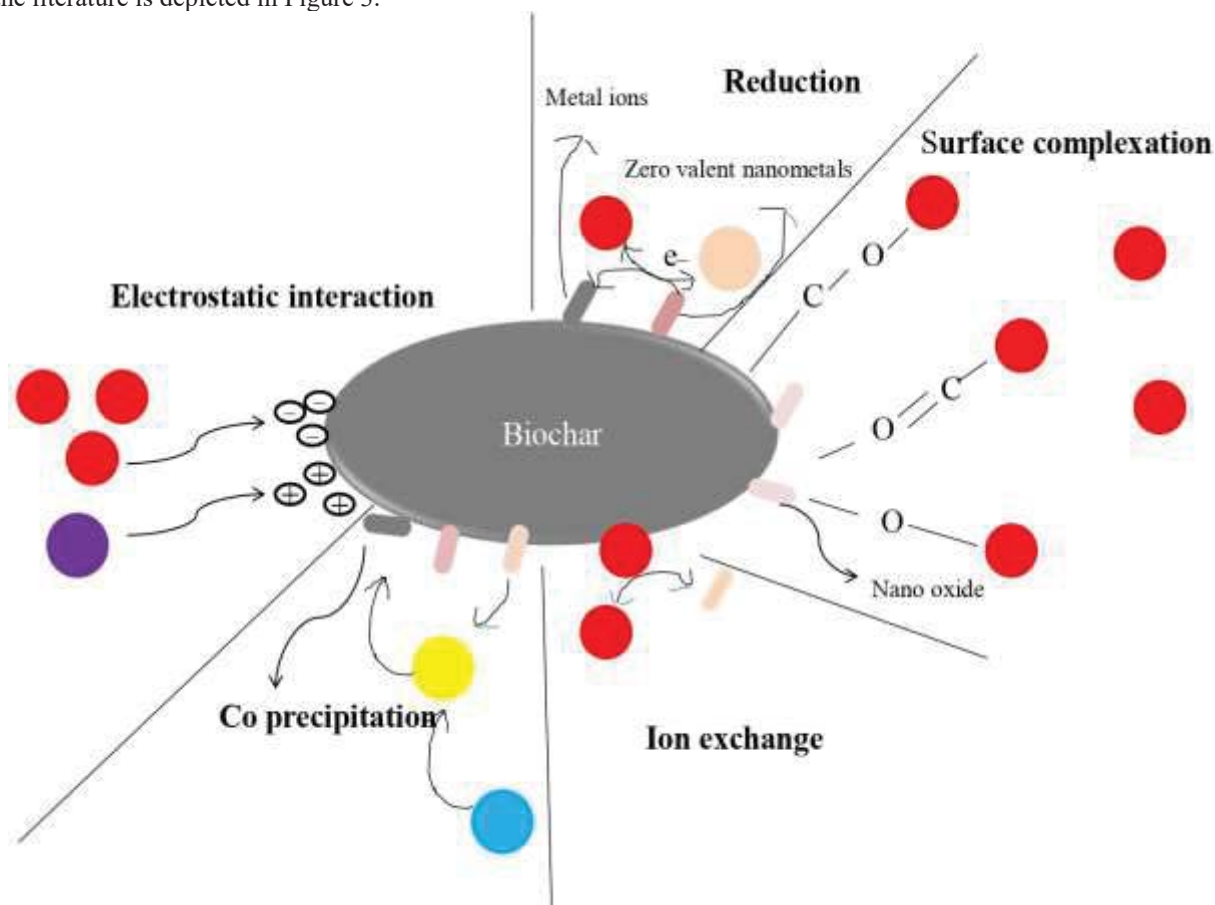


FIGURE 3. Mechanistic representation of removal of heavy metals from water

Co-precipitation

The mechanism of adsorption of Cr(VI) on the biochar incorporated with nanoscale zero valent ion (NZVI) analysed by XRD after and before the adsorption. Before the adsorption a peak of Fe(0) is observed which is disappeared after the adsorption. After the adsorption XRD analysis reveals that existence of FeO(OH), Cr₂O₃, Cr₂FeO₄ and Fe₃O₄, that are not appeared before the adsorption and it was indicated that occurrence of redox reaction nZVI particles with Cr(VI). In addition to this appearance of mixed chromium iron oxide compound (Cr₂FeO₄) which was results from co-precipitation of Cr(III) and Fe(III) oxides/hydroxides. The alteration of surface element chemical states after Hg(0) elimination through Fe₃O₄ nanoparticles loaded biochar has been recognised with XPS spectroscopy. It was found that Fe³⁺ coordination in Fe₃O₄ nanoparticles provided as oxidation and active adsorption site for Hg(0) [15]. The amount of O₂ enhanced from 36.3 to 47.5%, after oxidation from Hg(0) to Hg(II), the adsorbed Hg could convert into HgO and Hg-Fe precipitation. In addition to this adsorption of Cr(VI) on FeS nanoparticles loaded biochar, the surface heterogeneity and complexation can be observed by the generation of Cr(III)-Fe(III) complexes and Cr₂O₃/Cr₂S₃ precipitation [16].

Surface Complexation

The generated functional groups have been shown higher affinity towards heavy metals ions to form metal-ligand complexes. For example in the elimination of As(V), there is formation of inner sphere complexation between them [As(V) at pH=4.1], the -OH obtained from the nZVI Nanoparticles to the surface of biochar [17]. Further Neeli et al. [18] indicating the adsorption of As(V) on the nanoparticle assisted cellulose biochar occurred through surface complexation mechanism. The inner-sphere bidentate was formed with nZVI.

Reduction

The intermediate valent state for multivalent heavy metals would be achieved by the reduction reactions. The consequence reduction in heavy metals ions biotoxicity via reduction reactions and low valent ions produced can be stabilized via mineralization or precipitation [19]. As Fe(0) act as electron donor various heavy metals, therefore the iron or iron oxides nanoparticles seeking more attention. Furthermore, Yu et al. [20] suggested that the reduction was the predominant mechanism involved in the adsorption of Cr(VI) on a ZnO nanoparticle assisted biochar (obtained from waste water hyacinth). The EDX spectral analysis of ZnO/BC after the reaction revealed the existence of chromium and XRD analysis indicating that the uniform distribution of carbon, chromium and zinc. The XPS analysis after the reaction revealed that 90.6% Cr(III) was removed, which confirmed that reduction of Cr(VI) to Cr(III) during the adsorption process.

Ion Exchange

Neeli et al. [18] observed that the removal of Cu(II) occurred by ion exchange mechanism the nanoparticle assisted cellulose biochar. The peaks of the carboxylic and hydroxyl in the oxygen (O) disappeared, that indicating that involvement of ion exchange during adsorption process.

Electrostatic Interaction

Zhu et al. [21] observed that the removal of Cr(VI) occurred by electrostatic interaction mechanism on hematite nanoparticle biochar. The adsorption capacity of the Cr(VI) directly related with pH, which confirmed that the electrostatic interaction was involved in the adsorption of Cr(VI). If the pH value increases from 1 to 10 the adsorption reduced to 96.47% to 16.21%.

CONCLUSION

Biochar is the best alternative to apply as adsorbent for the removal of heavy metals ion due to its low cost and environment friendly nature. The efficiency of the biochar can be enhanced by loading the nanoparticle on the surface of the biochar which can alter their physiochemical properties such as shift of surface functional groups surface charge and formation of graphite shape. The removal of heavy metals ions on the nanoparticle loaded biochar can be elucidated via different mechanism such as co-precipitation, surface complexation, ion exchange, electrostatic interaction and reduction.

ACKNOWLEDGMENTS

Authors would like to thank Chitkara University Solan, Himachal Pradesh 174103 (India), for his valuable support and the research facility for writing this research paper.

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