

## Removal of Iron and Manganese from Ground Water by making use of Low-Cost Adsorbents

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### ABSTRACT

Sustainability of good health depends upon the purity of water. However groundwater may be exposed towards to contamination by various anthropogenic activities such as agricultural, domestic and industrial. Groundwater quality problem are typically associated with high level of iron concentration.

Iron is a worldwide observed public health problem. One of the major sources of iron is drinking water. Excess concentration of iron creates major issues related to the public concerned. The acceptable limit of iron is 0.3 mg/L according to the guidelines WHO guidelines. In developing countries like India removal cost of metal ions like iron is the major factor of consideration. Adsorption is one of the cost effective method adopted globally because of its ease to use and preparation. This review focused on the different used adsorbents for the removal of iron by using method of adsorption. Utility of different material of various plants, agro- wastes, other bio-masses as bio adsorbents are over viewed with its different parameter.

Keywords: removal of iron and manganese from water, Column Adsorption, natural materials, Vachellia Nilotica, Drinking Water

### Chapter 1

#### INTRODUCTION

Iron & Manganese are the most abundant transition metal in the earth's crust. Biologically it is the most important nutrient for most living creatures as it is the cofactor for many vital proteins and enzymes. Iron & Manganese mediated reactions support most of the aerobic organisms in their respiration process. If it is not shielded properly, it can catalyze the reactions involving the formation of radicals which can damage biomolecules, cells, tissues and the whole organism.

Adsorption is a technique for separating substances from gas or liquid phase onto surface of adsorbent. This is one of the methods for selective separation mechanisms in which it adsorbs one or more components from the mixture on a surface. Materials used to adsorb components are called as adsorbent while adsorbate is the component that being adsorbed. Adsorbent can be classified as synthetic adsorbent, natural adsorbent and semi-synthetic adsorbent. Synthetic adsorbent is most popular adsorbent used for researcher because of high adsorption capacities but, highly in cost production. Natural adsorbent such as plant, flower and leaf give very low cost production but also give low adsorption capacity. While the semi-synthetic adsorbent that can be define as natural material combining with chemical that possess high adsorption capacity and low cost compared to There is

common adsorbent have been extensively studied and commercialized such as silica gel, activated alumina and activated carbon. Activated carbon is the main adsorbent that are used for the water treatment. Researchers came out with idea of using activated carbon due to its simplicity and ability to remove broad ranges of pollutants with lower cost. Not limited to small scale focus, researchers also conducted study on activated carbon usage for waste streams purification. Materials for activated carbon usually have a high percentage of carbon and the adsorption capacity varies depending on their porous structure. In addition, it should be noted that characteristics of carbon precursor and techniques during synthesis including the experimental condition have significant effect to the final pore size distribution for activated carbon. The various adsorbent study is sawdust [7], carbon aerogel, herbaceous peat, fly ash, modified clay, activated carbon-zeolite composite and many more.



*Croton gibsonianus* (Euphorbiaceae), Babul (*Vachellia nilotica*), Parosa Pimpal (*Thespesia populnea* soland), Eraka (*Typha elephantina*), Abhali (*Cynotis tuberosa*), Abolima (*Murdannia Lanuginosa*) were used to adsorb Fe and Mn ions from water sources. The effects of parameters such as contact time, composition percentage, and particle size of biosorbents in a fixed-bed adsorption column were investigated. The study on the adsorption of Fe and Mn ions showed that the amount of adsorption increased significantly by decreasing the particle size. Furthermore, Iron and Manganese are two metals commonly found in wells water. This is also due to the presence of a rocky bed in the groundwater, causing excessive metal taste and stains. The permissible level of Mn is 0.5 mg/l. Drinking water standards set the maximum allowable amount of iron at 0.3 mg/l, because higher levels are undesirable for industrial and domestic use. Due to environmental and health issues, the removal of Fe and Mn ions from water resources by surface adsorption and a low-cost adsorbent has been discussed. Among various methods available for removal of metallic elements, the adsorption process is preferred owing to its flexibility, high efficiency, reproducibility and being economical. Natural or modified biomaterials, by-products, or waste from industrial and agricultural operations are the most important sources of low cost adsorbents. Most studies on the removal of metal ions in surface and groundwater are performed using a batch system, which is generally and easily applicable in laboratory studies and limited to the processing of water sources in small quantities. In a batch system, the equilibrium time is short, and in a continuous system, the adsorbent is always in the vicinity of the fresh solution, the experiments were performed in a fixed bed column; the effect of adsorbent dose, initial concentration, pH, and particle size and breakthrough curves was assessed. Fig 1- Water with Fe & Mn and Clear Water.

### 1.1 Iron and manganese in groundwater

Sources of iron and manganese Iron and manganese are common metallic elements that occurs together naturally especially in deeper wells with little or no oxygen present. Natural sources of iron and manganese may include weathering of iron and manganese bearing minerals like amphibole, iron sulfide and iron rich clay minerals. In areas where groundwater flows through an organic rich soil, iron and manganese will also dissolve in the groundwater. Iron and manganese can also have anthropogenic sources including industrial effluents, landfill leakages and acid mine drainage. Well casing, pump parts, piping and storage tank can also contribute iron and manganese to groundwater (Nova Scotia, 2008). In natural conditions, water percolates through the organic soil where dissolved oxygen is consumed by the decomposition of organic matter and microbes in the soil. The decomposition process reduces the pH due to the microbial action. In combination with the lack of oxygen, the iron and manganese atoms are also reduced from  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$  to  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ . The most dominant form of dissolved iron is the soluble  $\text{Fe}^{2+}$  under the pH range of 5 to 8. When groundwater is pumped up to the surface it gets into contact with air ( $\text{O}_2$ ) which enters the solutions and starts the oxidation process that releases carbon dioxide ( $\text{CO}_2$ ) from the groundwater to the atmosphere. When this happens, the pH values are increased and hence the  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  are changed into the insoluble  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$  minerals.

### 1.2 Forms of Occurrence of Iron and Manganese in Water

Iron and manganese occur in dissolved forms as single ions ( $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ) or in undissolved higher forms mainly as  $\text{Fe}(\text{OH})_3$  or  $\text{Mn}(\text{OH})_4$ , respectively. They can also be present in colloid form (bound to humic substances). The form of their occurrence depends on oxygen concentration, solubility of Fe and Mn compounds in water, pH value, redox potential, hydrolysis, the presence of complex-forming inorganic and organic substances, water temperature, and water composition (e.g.  $\text{CO}_2$  content).

### 1.3 Effect on Water Quality

Adverse effects of higher Fe and Mn concentrations in drinking water can be summarized as follows: 1. iron (II) and manganese (II) ions are oxidized to higher forms in a water distribution system and this results in the formation of hydroxide suspensions causing undesirable turbidity and colour of water, 2. the presence of iron and manganese bacteria in water supply system causes change in water quality (smell) and bacterial growth in pipes, 3. in the case of the occurrence of iron (II) and manganese (II) ions at the consumer's point, iron and manganese are oxidized and precipitated under suitable conditions (e.g. in washing machines, boilers). Following the above-mentioned facts, higher concentrations of iron and manganese in water cause technological problems, failure of water supply systems operation, water quality deterioration and, in water with slightly higher concentrations of oxygen, they form undesirable incrustations that result in the reduction of pipe flow cross-section.

### 1.4 Manganese Ore :

- 1) Manganese ore deposits occurring in Central India are supposed to be the most promising deposits in the Country.
- 2) The chief ore deposits in Maharashtra occur as an arcuate belt passes through Kandri-Mansar area of Nagpur district, which forms the middle portion of the belt- Dongri Budruk and Sitasaongi in Bhandara district.
- 3) Almost all Manganese ore production of the State comes from Nagpur and Bhandara.
- 4) Small occurrences of low grade manganese ore are found in Sindhudurg district.
- 5) The total reserves of manganese ore in the State are estimated at 20.85 million tonnes
- 6) Mostly utilized in the manufacture of ferromanganese, silicomanganese and iron and steel industries and to a small extent in production of battery cells.

### 1.5 Iron Ore

- 1) Important iron ore occurrences in the State are confined to the districts of Gadchiroli, Chandrapur, Gondia and Sindhudurg.
- 2) Out of the total estimated reserves of 260.824 million tonnes of iron ore, the Gadchiroli district

alone accounts for 178 million tonnes, the rest 75.38 million tonnes being from areas of Sindhudurg & 2.18 million tonnes Chandrapur districts. 3) The iron ore deposits around Surjagarth in Etapalli tahsil of Gadchiroli district is the biggest deposit in the State.

## **1.6 AIM AND OBJECTIVE**

### **1.6.1 AIM**

Remove the Iron and Manganese from the water by Absorptive Media of char prepared from barks of Parosa Pimpal (*Thespesia populnea* soland), Pophali (*Areca catechu*) Abhali (*Cynotis tuberosa*) By using

- i) Column Adsorption

### **1.6.2 OBJECTIVES**

- a. To Study the behavior and availability of *Vachellia Nilotica* & *Thespesia Populnea Soland*.
- b. Design & development of Activated charcoal from Identified species
- c. Application of prepared PAC to remove Fe, Mn.
- d. Validation of prepared Results.

## **Chapter 2**

### **LITERATURE REVIEW**

#### **2.1 What Is Literature Review**

Studied the Literatures which will give Activated charcoal prepared from the locally available Plants and trees as it is very essential in both the batch and column processes.

#### **2.3 Research papers and their reviews**

- i) Adsorption studies of cationic dyes onto Ashoka (*Saraca asoca*) leaf powder

In present study by Neha Gupta and Mahesh chandra, batch adsorption experiments were carried out using ashoka leaf powder (ALP), a low cost, locally available biomaterial as an adsorbent for the removal of cationic dyes such as methylene blue, malachite green, rhodamine B and brilliant green from aqueous solution. The ALP was characterized by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscope (SEM). Effect of various physico-chemical parameters such as pH, ionic strength, adsorbent dose, contact time, initial dye concentration and temperature were investigated and optimal experimental conditions were ascertained. Available models like Lagergren's pseudo-first order kinetics, Ho's pseudo-second order kinetics and intraparticle diffusion were used to evaluate the kinetics and the mechanism of the adsorption. The Langmuir, Freundlich, Temkin and Scatchard isotherm models were tested to represent the equilibrium data and the constants of the isotherms were determined by using the experimental data. Thermodynamic parameters such as change in Gibbs free energy ( $\Delta G^\circ$ ), change in enthalpy ( $\Delta H^\circ$ ) and change in entropy ( $\Delta S^\circ$ ) were calculated to predict the nature of adsorption process.

- 2) Onion (*Allium Cepa*) Processing Waste as a Sorption Material for Removing Pollutants from Aqueous Media by Ildar G. Shaikhiev, Natalia V. Kraysman, Svetlana V. Sverguzova

The paper summarizes the literature data on the use of onion (*Allium cepa*) processing waste as sorption materials to remove various pollutants (metal ions, dyes, antibiotics) from aqueous media. It provides brief literature data on the structure, volume of cultivation, and chemical composition of some components of onion biomass. It was found that onions contain many amino acids, vitamins, polyphenolic compounds, and other biologically active

compounds that have various functional groups in their composition. This contributes to the removal of various metal ions ( $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr(VI)}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ) from aqueous media with native and modified onion processing waste (onion skin). The work shows the possibility of increasing the sorption characteristics of pollutants by treating the *Allium cepa* biomass with various chemical reagents. It was found that the pollutant adsorption isotherms on onion skin are most often more accurately described by the Langmuir and Freundlich models, less often by other models. The kinetics of the process predominantly corresponds to the pseudo-second-order model. It was shown that the use of onion skin extracts modified with various chemical compounds is promising for removing heavy metal ions. The work also shows the possibility of using onion skin modified by plasma and microwave radiation to remove the Methylene blue dye from simulated solutions.

3) Adsorption Characteristics of Anthocyanin's from Purple-fleshed Potato (*Solanum tuberosum* Jasim) Extract on Microporous Resin Xuan Liu, Zhenghong Xu, Yangxiang Gao, Bin Yang, Jian Zhao and Lijun Wang proved that The adsorption characteristics of anthocyanins from purple-fleshed potatoes on 11 macroporous SDVB, acrylic and methacrylic resins were investigated. Anthocyanins were first extracted from purple-fleshed potatoes using dilute acid solutions, and then partially purified by membrane filtration, which resulted in the removal of more than 90% of the total sugar and proteins from the crude extract. The partially purified extract were mixed with the resins at varying extract/resin ratios until equilibrium adsorption was reached and the adsorption data were fitted to the Langmuir and Freundlich isotherms. Both models were found suitable to describe the adsorption isotherms of anthocyanins on the resins tested. Adsorption capacities for anthocyanins increased with the rise of temperature for SDVB resins but decreased for methacrylic resins. The resin with the highest adsorption capacity for anthocyanins was XAD-1600, on which anthocyanin adsorption was an endothermic process and favored at higher temperature.

4) Preparation and characterization of a novel adsorbent from *Moringa oleifera* leaf by Olugbenga Solomon Bello, Kayode Adesina Adegoke & Opeyemi Omowumi Akinyunni

Has proved that A new and novel adsorbent was obtained by impregnation of *Moringa oleifera* leaf in  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ , respectively. Prepared adsorbents were characterized using elemental analysis, FT-IR, SEM, TGA and EDX analyses, respectively. The effects of operational parameters, such as pH, moisture content, ash content, porosity and iodine number on these adsorbents were investigated and compared with those of commercial activated carbon (CAC). EDX results of acid activated *M. oleifera* leaf have the highest percentage of carbon by weight (69.40 %) and (76.11 %) by atom, respectively. Proximate analysis showed that the fixed carbon content of acid activated *M. oleifera* leaf ( $69.14 \pm 0.01$ ) was the highest of all adsorbents studied. Conclusively, the present investigation shows that acid activated *M. oleifera* leaf is a good alternative adsorbent that could be used in lieu of CAC for recovery of dyes and heavy metal from aqueous solutions and other separation techniques.

5) Inhibitory Efficacy of *Croton gibsonianus* Nimm. Grah (Euphorbiaceae) Against Oral Isolates of *Streptococcus mutans* by Prashant Kekuda T.R and Venugopal T.M explained that The present research was undertaken to investigate the anticariogenic activity of methanol extract of *Croton gibsonianus* Nimm. Grah (Euphorbiaceae) leaves. The shade dried leaves were powdered and extracted with methanol. The inhibitory efficacy of methanol extract was tested against 24 oral isolates of *Streptococcus mutans* by Agar well diffusion method. The extract caused a dose dependent inhibition of cariogenic isolates. Preliminary phytochemical analysis showed the presence of saponins, glycosides, tannins and terpenoids. The inhibitory efficacy of extract against cariogenic isolates could be due to the presence of these metabolites. In suitable form, the plant could be used to treat dental caries. Further study is needed to identify the bioactive components and their efficacy against cariogenic bacteria.

6) Application of *Terminalia arjuna* as potential adsorbent for the removal of  $\text{Pb(II)}$  from aqueous solution: thermodynamics, kinetics and process design by Rifaqat Ali Khan Rao Explained that he present work explored the adsorption properties of *Terminalia arjuna* fruit powder for the removal of  $\text{Pb(II)}$  from aqueous solution. Effect of concentration, contact time, pH, adsorbent dose, and temperature were studied using batch

process to optimize conditions for maximum adsorption of Pb(II). Kinetic data showed that the pseudo-second-order model was the best fit for the experimental data over a wide range of concentrations. Thermodynamic parameters ( $\Delta H^\circ$  and  $\Delta G^\circ$ ) suggested endothermic and spontaneous nature of adsorption. Mean free energies at different temperatures were in between 10.1 and 14.3 kJ mol<sup>-1</sup> indicating chemical nature of adsorption process.

Equilibrium isotherm data were analyzed using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherms models at 30, 40, and 50°C. The breakthrough and exhaustive capacities were found to be 5 and 15 mg g<sup>-1</sup>, respectively. Desorption studies were carried out by column method and 84% of Pb(II) ions were recovered when

0.05 N HCl was used. A single-stage batch adsorption design was proposed to predict the amount of adsorbent required for 98% removal of Pb(II) from different volumes of water.

7) Health Risk Assessment of Groundwater Iron and Manganese in Chandrapur District, Central India by Rahul K. Kamble explained that Chronic daily intake, hazard quotient and hazard index were very low for these heavy metals which indicate inhabitants of the study area were no immediate or remote health threat from ingestion of this groundwater.

## 2.4 FINDING FROM LITERATURE REVIEW

- 1) GAC, PAC prepared Agricultural waste good for removal of the heavy metals from the groundwater such as Ar, Cr, Pb, Fe, Cu, Mn, Hg, Zn etc.
- 2) Batch Adsorption is good for some charcoals and column adsorption is good for some charcoals.
- 3) Ion exchange, Lime Precipitation is quite costlier methods for carrying out the treatment for removal of the Fe & Mn.
- 4) Poor and Tribal peoples cannot use such technique in their life, due to more cost, lack of knowledge of handling it.
- 5) Need to develop a method which can give low spending's and material those we are using are locally available.

## CONCLUSION

Column Adsorption by using Activated charcoal prepared from Vachelia Nilotica, Hydrated lime, Alum, Aloe Vera is efficient in removal of Excess Iron and Manganese present in ground water. and then after treatment water can be used for drinking and other purposes.

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