International Journal of Engineering Research
Volume No.4, Issue No.3, pp : 111 - 114

ISSN:2319-6890)(online),2347-5013(print)
01 March. 2015

Manganese Removal by Low Cost Adsorbent from Synthetic Wastewater-A Review

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Abstract : ***Manganese (Mn) is one of the most abundant metals in Earth's crust. Manganese is present in ground water as a divalent ion (Mn^{2+}) and is considered a pollutant mainly because of its organoleptic properties. It is an essential metal for the human system and many enzymes are activated by manganese. Therefore, manganese has to be removed from some waters and wastewaters for various reasons. Conventional chemical and physical treatments for Mn(II) removal from contaminated effluent consist of precipitation, depth filtration, ion exchange, adsorption and oxidation. The adsorption technique has been found to be one of the most effective for the removal of metal ions from solution. This review focuses on preparation of adsorbent by using of low cost material to remove manganese from wastewater.***

Keywords: Manganese removal, Toxic, Low cost adsorbent, Adsorption, Isotherms.

1. Introduction

Presence of Manganese in ground water

Manganese is a very common compound that can be found everywhere on earth. Groundwater is a main source of drinking water and the soluble Mn(II) often exceeds WHO standard. It is present in the atmosphere as suspended particulates resulting from industrial emission, soil erosion, and volcanic emissions (Su et. al., 2014). It is an essential metal for the human system and many enzymes are activated by manganese. Manganese has a variety of applications in ceramics, primary cells (dry battery), and electrical coils. Manganese is an essential element for human health. Shortages of manganese can also cause health effects like fatness, glucose intolerance, blood clotting, skin problems, lowered cholesterol levels, skeleton disorders, birth defects, changes of hair colour, neurological symptoms. Manganese is also used in alloying element of many alloys (Akpomiea and Dawodu, 2014).

1.1 Awful effects of Manganese

Manganese is one out of three toxic essential trace elements. This means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in human body. Manganese effects occur mainly in the respiratory tract and in the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese in particular is considered a pollutant mainly because of its organoleptic properties in high concentrations, it causes neurological disorders and brain damage.(Meitei and Prasad, 2014)

This heavy metal causes corrosion and pipe blockages (directly by precipitation or indirectly by creating favorable growth conditions). Manganese affects the appearance of the water and imparts a metallic taste to the water. This problem causes laundering difficulties and poses a potential pollution problem to the receiving watercourse. All in all, particular problems may be experienced with ground water having a high Mn^{2+} content. Also, The precipitate on contact with air and turn dark brown or black color, creating obvious problems.(Ates, 2014)

1.2 Treatment Techniques

Naturally occurring Mn(II) is commonly found in drinking water sources and is essential for human health at low concentrations. On the other hand, excessive ingestion of Mn(II) can result in respiratory, reproductive, and especially neurological adverse effects for human beings. According to World Health Organization (WHO), a Mn(II) concentration of 0.05 mg/L in drinking water is usually acceptable to consumers. The permissible limit of Mn (II) in drinking water as set by the World Health Organization (WHO) is 0.4 mg/l. (Taffarel and Rubio, 2009). This thesis will cover the removal of manganese by use of different type of low cost adsorbent The acceptable and permissible limits of manganese in drinking water is given in Table 1.

Table 1:Bureau of Indian Standard (IS 10500-2012)

Element	Acceptable limit	Permissible limit
Mn(mg/l)	0.1	0.3

Several techniques have been used to remove heavy metals from effluents, such as oxidation, coagulation–flocculation, membrane filtration, sedimentation, solvent extraction, ion exchange, reverse osmosis, evaporation, reduction and adsorption (Ganesan and Kamaraj, 2012). Most of these processes, however, are expensive, inefficient and inapplicable to a wide range of pollutants and toxic wastes that are difficult to treat. Adsorption is the generally preferred method for removing heavy metal ions in terms of initial cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants and the availability of different adsorbents. Furthermore, it does not result in the formation of harmful substances, a problem with most other methods. Although activated carbon has been the substance of choice for treating

ISSN:2319-6890)(online),2347-5013(print)
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wastewater containing heavy metals, because of its good adsorption, it is expensive, which limits its wide spread use. As a result, many scientists have sought cheaper alternatives (Bosco et. al., 2006).

2. Literature Review

Potgieter et. al.,2004, studied the use of ferrichloride as coagulant in conjunction with hydrogen peroxide as an oxidant and different physical treatment processes, such as adsorption and nanofiltration, to reduce dissolved iron and manganese in water with a high DOC loading. Use of ferrichloride as coagulant in conjunction with hydrogen peroxide as an oxidant and different physical treatment processes, such as adsorption and nanofiltration, to reduce dissolved iron and manganese in water with a high DOC loading.

Bosco et. al., 2006, Investigated the process of sorption of manganese(II) and cadmium(II) present in synthetic aqueous effluents, by calculating the adsorption isotherms at 298 K using batch experiments. Adsorption of metals was best described by a Langmuir isotherm. We observed two distinct adsorption mechanisms that may influence adsorption. At the first 5 min of interaction, a cation exchange mechanism that takes place at exchange sites located on basal planes is predominant. This process is inhibited by low pH values. After this first and fast step, a second sorption mechanism can be related to formation of inner-sphere surface complex, which is formed at edges of the clay. The results have shown that both Cd(II) and Mn(II) were totally retained from a 50 mg L^{-1} solution when K10 grafted with ammonium pyrrolidinedithio-carbamate (APDC) was used as adsorbent. The APDC-modified clay showed higher affinity for cadmium(II) and manganese(II), promoting total retention when the initial concentration was 50 mg L^{-1}.

Sharma et. al.,2007, investigated on waste material of thermal power plants for the removal of manganese from aqueous solutions and wastewaters. The removal was found to be highly concentration dependent and higher removal (%) was obtained at low concentrations of Mn(II) in the solutions. The removal decreased from 74.2 to 47.2% by increasing the Mn(II) concentration from 1.5 to 5.0 mg l^{-1} at 298 K, pH 8.0, and 1.0×10^{-2}M $NaClO_4$ ionic strength. Removal, however, decreased from 51.3 to 7.2% by increasing the adsorbent particle size from 100 to 250 m. Thermodynamic parameters namely free energy, G◦, enthalpy, H◦, and entropy,S◦ were calculated. Fly ash can be successfully used for Mn(II) removal. The removal is highly dependent on initial concentration of Mn(II) in solution and higher removal (%) has been observed in lower concentration ranges. Rate constant of adsorption was found to be 2.12×10^{-2} ks^{-1}.The data obtained can serve as background data for designing treatment plants for treatment of Mn(II) wastewater economically. Though a detailed cost analysis is yet to be carried out, process of removal seems to be economically viable suitable for developing nations like India.

Taffarel and Rubio, 2009, investigated the zeolite sample, composed mainly of clinoptilolite and mordenite. The adsorption onto the activated zeolite followed the pseudo-second-order kinetic model and activation of the Ch-zeolite with NaOH resulted in the highest reaction rate. The equilibrium data showed excellent correlation with the Langmuir isotherm model. Results shows that the natural Ch-zeolite had a high specific surface area (118 m^2 g^{-1}), the particles were negatively charged and presented a cation-exchange capacity of 1.09 meq NH_4^+ g^{-1} . Mn^{2+} ion adsorption onto activated Ch-zeolites was adjusted to four kinetic models, but only the pseudo-second-order kinetic model showed a good fit and NaOH activated Ch-zeolite reached the highest reaction rate. The Langmuir isotherm model, showed the best correlation to the equilibrium Data. Results also showed that the cation-exchange capacity of the activated zeolites increased in relation to natural zeolite and that the different activation procedures had an important role in the adsorption process.

Mohan and Gandhimathi, 2009, investigated the possibility of the utilization of coal fly ash as a low cost adsorbent material for the adsorption of heavy metal ions (Zn, Pb, Cd, Mn and Cu) present in the municipal solid waste leachate. Batch experiments were conducted to determine the effect of contact time and fly ash dosage on adsorption of heavy metals. Experimental data were evaluated to find out kinetic characteristics of the adsorption process. The isothermal data could be well described by the Freundlich adsorption model. Kinetic parameters of adsorption such as the pseudo first-order constant, pseudo second-order constant and the intraparticle diffusion rate constant were determined. The fly ash concentration required to achieve maximum heavy metal removal was found to be 2 g/L with the removal efficiencies of 39%, 28%, 74%, 42% and 71% for Cu, Mn, Pb, Zn and Cd respectively. The results of the study demonstrated that the fly ash could be used as an effective low cost adsorbent for the removal of heavy metal ions from municipal solid waste leachate.

Pirajan et. al.,2010, synthesised activated carbon from coconut shells (ACCS) and used it for the removal of metal ions. Adsorption capacities were determined: copper ions exhibited the greatest adsorption on activated carbon obtained from coconut shells because of their size and pH conditions. Adsorption isotherms from aqueous solutions of heavy metals on ACCS were determined and were found to be consistent with Langmuir's adsorption model. Adsorbent quantity and immersion enthalpy were studied. From the experiments, it can be concluded that the activated carbon obtained from coconut shells has an excellent ability to retain Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^2 metal ions from aqueous solutions at studied concentrations. This adsorption is described by an isotherm of type I and is fully verified by the Langmuir isotherm. The kinetics of the manganese, iron, nickel and copper adsorption on the ACCS was found to follow a pseudo-second-order rate equation. This method is advantageous as it can be applied to countries where the residue of coconut is a problem.

Omri and Benzina, 2012, prepared activated carbon from Ziziphus spina-christi seeds (ZSAC) to remove Mn(II) from aqueous solutions to characterize the adsorptive characteristics of the produced active carbon. Adsorption experiments were carried out by batch experiments. The adsorption equilibrium data were analyzed by Langmuir, Freundlich and Temkin isotherm models. They concluded that maximum adsorption capacity of manganese calculated from Langmuir isotherm was around 172 mg/g. The equilibrium adsorption of Mn(II) over the entire concentration range was best described by the Freundlich isotherm, as indicated by the high values of the correlation coefficients ($R^2 = 0.984$).

Ganesan and Kamaraj, 2012, applied a batch adsorption process to investigate the removal of manganese from aqueous solution by oxidized multi walled carbon nanotubes (MWCNTs). In doing so, the thermodynamic, adsorption isotherm, and kinetic studies were also carried out. A systematic study of the adsorption process was performed by varying pH, ionic strength, and temperature. Manganese-adsorbed MWCNT was characterized by Raman, FTIR, X-ray diffraction, XPS, SEM, and TEM. The experimental results indicate that MWCNT can effectively remove manganese in an aqueous solution. The percentage of manganese removal by MWCNT can reach 96.82 %. Kinetic studies suggest that the equilibrium is achieved only within 354 min and the pseudo-second-order model is followed. The adsorption isotherms could be well fitted by the Langmuir adsorption isotherm equations. Temperature studies showed that adsorption was endothermic and spontaneous in nature.

Ma et. al., 2013, studied the use of Pleurotus ostreatus (P. ostreatus) nano-particles (PONP) as a new nano-biosorbent to remove Mn(II) from aqueous solution. Adsorption experiments were carried out by batch experiments to investigate the effects of different experiment parameters. The adsorption equilibrium study exhibited that Mn(II) adsorption of PONP was better fitted by Langmuir isotherm model. The maximum Mn(II) adsorption capacity of PONP was 130.625 mg/g at 298.15 K, which was higher than many other adsorbents. Pseudo-second-order kinetic model was the best one to predict the sorption kinetics with a maximum adsorption capacity of PONP attained within 30 min. PONP showed great potential in wastewater treatment due to the high adsorption capacity.

Qomia et. al., 2014, studied the adsorption of manganese ions from aqueous solution by polyaniline/sawdust nano-composite. The experiments were conducted to evaluate the effect of various experimental parameters i.e., pH, adsorbent dosage and contact time on the removal efficiency. The experimental results have been analyzed using a pseudo-Langmuir adsorption isotherm and a pseudo-Freundlich adsorption isotherm models. The results showed that optimum conditions for manganese removal were found to be at pH 10, adsorbent dosage of 10 g/L and equilibrium contact time of 30 min. According to the evaluation using the pseudo-Freundlich model, the monolayer adsorption capacity (qmax) of PAn/SD for manganese ions was obtained to be 58.824 mg/g.

Ates, 2014, investigated the natural zeolite (NZ) obtained from Sivas-Yavu of Turkey and modified by ion-exchange (NH_4NO_3), alkali treatment (NaOH) and addition of aluminum ($Al_2(SO_4)_3$). The natural and modified samples were characterized. Ion-exchange with NH_4^+ of NZ results in the exchange of the Na^+ and Ca^{2+} cations and the partial exchange of the Fe^{3+} and Mg^{2+} cations. While the treatment of the NZ with NaOH leads to insignificant change of almost all cations, it causes significant dealumination and desilication of the NZ. FTIR and TGA results showed that decationization, dealumination and desilication give rise to a decrease in hydrophilic nature of NZ. However, manganese adsorption of samples enhances their hydrophilic nature. All modifications, ion exchange, alkali treatment, and aluminum introduction, increased two times the manganese adsorption capacity of natural zeolites. The Freundlich isotherm model was best fitted to the isotherm data obtained due to a heterogeneous surface existence.

Cavalcante et. al., 2014, performed Column absorption tests in order to compare the manganese sorption behaviour of an Italian coal fly ash and zeolite synthesised from it. Different masses of both materials were exposed to solutions containing a total metal concentration of 10 mg/L. Batch adsorption studies were also conducted to determine the effect of time on the removal on Mn sequestration. The results indicate that both materials are effective for the removal of Mn from aqueous solution by precipitation due to the high pH of the solid/liquid mixtures. However, the leaching tests reveals that the amount of Mn removed from the fly ash was greater than that leached from the zeolite, thereby indicating that the metal is partially sequestrated by zeolite.

Akpomiea and Dawodu, 2014, explored alkaline-activated montmorillonite as a low-cost adsorbent for simultaneous removal of Ni(II) and Mn(II) ions from solution. The experiment was performed by batch adsorption. Alkaline modification of montmorillonite increased the specific surface area from 23.2 to 30.7 m^2/g and the cation exchange capacity from 90.78 to 94.32 mEq/100 g. The adsorption capacity of the montmorillonite for Ni(II) and Mn(II) ions increased with alkaline modification. When four isotherms, the Langmuir, Freundlich, Temkinand Dubinin–Radushkevich models, were applied to the experimental data, the best fit was obtained with the Freundlich model. The kinetic data were analysed with pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion rate equations; greater conformity was found with the Elovich equation. Thermodynamic studies revealed a spontaneous, endothermic physical adsorption process. The results show that alkaline modification of montmorillonite enhances its adsorption capacity for Ni(II)and Mn(II) ions. The heterogeneous nature of the alkaline-modified clay was revealed by the good fit of the data to the Freundlich model, while thermodynamic studies revealed endothermic, spontaneous physical adsorption. These results indicate that alkaline-modified montmorillonite clay is potentially a low-cost adsorbent for the removal of Ni(II)and Mn(II) ions from solution.

Meitei and Prasad, 2014, studied the potential of the free floating freshwater macrophyte Spirodela polyrhiza (L.) Schleiden from the phoomdi of Loktak lake, India as an adsorbent to remove Cu (II), Mn (II) and Zn (II) ions from single, binary and ternary metal solution system was investigated. Langmuir isotherm best described the equilibrium with maximum adsorption capacities (qmax) of 52.6 mg g^{-1} for Cu (II), 35.7 mg g^{-1} for Mn (II) and 28.5 mg g^{-1} for Zn (II) ions.

The adsorption efficiency for Cu (II), Mn (II) and Zn (II) ions was found to be significantly higher as compared to reported biomasses. Maximum adsorption capacities of 52.6 mg g^{-1} for Cu (II), 35.7 mg g^{-1} for Mn (II), and 28.5 mg g^{-1} for Zn (II), respectively were achieved at the optimized conditions. The sequence of affinities between the biomass and the metal ions was as follows: copper > manganese > zinc.

Dawodua and Akpomiea, 2014, investigated an unmodified Nigerian kaolinite clay (UAK) as a low-cost adsorbent for the removal of Ni(II) and Mn(II) ions from a binary solution of both metal ions. Batch adsorption methodology was used. The equilibrium isotherm data were analyzed using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherm model. The Freundlich isotherm model provided the best fit to the experimental data for both metal ions. The Langmuir monolayer maximum adsorption capacities for Ni(II) and Mn(II) ions are 166.67 mg/g and 111.11 mg/g, respectively. Kinetic parameters were also analyzed using the Lagergren pseudo-first order, pseudo-second order, Elovich equation and intraparticle diffusion rate equation. The Elovich equation provided the best fit to the experimental data and the result also indicated the presence of intraparticle diffusion on the sorption of both metal ions, although it was not the sole rate determining step. Thermodynamic analysis showed that the process was spontaneous and endothermic in nature.

3. Conclusion

The discharge of heavy metal pollutants into the environment from sewage, industrial and mining waste effluents is a serious problem due to its impact on human health and natural environment. The development and application of effective treatment processes is necessary for the control of the metal toxicants. Adsorption is the popular technique for treating the wastewater containing manganese. This paper studies about the use of various low cost adsorbents and about the experiments carried out in this area by batch experiments to investigate the effects of different experiment parameters. The adsorption isotherms could be well fitted by the Langmuir adsorption isotherm equations. Temperature studies showed that adsorption was endothermic and spontaneous in nature.

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