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Removal of Copper (II) Ions from Aqueous Solution Using Manganese Oxide Nanopowder

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Abstract

Copper is a widely used metal for various applications such as electroplating, building applications, industrial machinery and the electronics industry. There is increasing concern about the environmental issues related to copper heavy metal in the wastewater produced by the copper mining industry. The present work focuses on treating copper (II) ions using manganese oxide (MnO_2) nanopowder. The MnO_2 nano-material was synthesised using the combustion process and characterised using X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). It was found that it mainly contained crystalline α-MnO_2. The effect of variables including the initial pH, contact time, initial concentration and adsorbent dose that influence the adsorption process was studied. Results showed that under best conditions, i.e., 500 mg/L initial concentration, 15 g/L absorbent dosage, 3 hours contact time, initial pH of 5.0 and a stirring speed of 120rpm, copper (II) was reduced to non-detectable levels. The high concentration of copper was reduced effectively by MnO_2 nanoparticles. Isotherm and kinetics of the adsorption process were studied. Kinetic data followed Ho's pseudo-second-order kinetics. This study indicated that MnO_2 nano-material has a tremendous potential to remove copper (II) ions.

Keywords: *Adsorption, Copper (II) Removal, Isotherm, Manganese Oxide.*

1.0 Introduction

Industrialisation and urbanisation have increased in the past few decades significantly. The consequence of this is an increase in manufacturing and product demand. Water, being an essential utility in most manufacturing processes, forms a significant part of effluents. These industrial effluents contain many toxic substances, mainly heavy metals such as Hg, Cu, Cr, Pb, Sb, Ni, Cd, etc. and hence have to be treated before disposing into the environment[1,2].

A common industrial metal, copper is used for roofing, plumbing, air conditioning, tubing and electrical wiring[3]. Owing to its wide range of applications, certain foods, including shellfish, liver, mushrooms, nuts and chocolate, may contain copper. Wilson's illness, which is characterised by hepatic cirrhosis, brain impairment and renal failure, is brought on by excessive copper consumption and exposure[4]. Since copper is the most widely used non-ferrous metal, copper mining plant capacity is higher than other heavy metal plants. Copper mining wastewater is the result of the excavation of copper deposits entering the water through the leaching of open mines and underground pits. Among various strategies explored by researchers for treating copper-containing effluents, adsorption was found to be the most effective.

In the present work, manganese oxide nanopowder was synthesised using combustion synthesis and characterised using XRD and SEM. The synthesised powder was utilised as an adsorbent to extract copper

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from the aqueous solution. The effects of several factors, including initial metal ion concentration, initial pH, contact time, and MnO_2 dosage, were investigated. Furthermore, kinetics was also studied to comprehend the adsorption mechanism.

2.0 Materials and Methods

2.1 Chemicals

All chemicals procured for experiments were of analytical grade. De-ionised water used was from the Millipore Milli-Q system. Manganese nitrate hepta hydrate $Mn(NO_3)_2.7H_2O$ was obtained from Merck. Copper sulphate pentahydrate $CuSO_4.5H_2O$ was obtained from NICE Chemicals Pvt. Ltd. By dissolving a predetermined quantity of $CuSO_4.5H_2O$ in water, 1000 mg/L of copper was prepared which was further diluted to the desired concentration.

2.2 Manganese Oxide Synthesis

Manganese oxide nanopowder was synthesised using combustion synthesis[5-7]. $Mn(NO_3)_2.7H_2O$ was mixed thoroughly with sugar as the fuel and water as the solvent in stoichiometric ratios as shown in Equation 1.

$$W_F = \frac{O_{MN}}{O_F} \times \frac{W_{MN}}{MW_{MN}} \times MW_F \quad (1)$$

Where W_F Is the weight of the fuel; O_{MN} is the oxidation number of manganese nitrate; O_F is the oxidation number of fuel (sugar); W_{MN} is the weight of manganese nitrate; MW_{MN} is the molecular weight of manganese nitrate and MW_F is the molecular weight of the fuel (sugar).

The mixture was placed in a muffle furnace open to the atmosphere and preheated to 400 °C. The water evaporated, leaving behind expanded liquid foam which eventually gave rise to a brown powder after cooling. The yield was calculated as shown in Equation 2 and it was found to be approximately 30% by weight.

$$\text{Yield} = \frac{MW_{MN}}{MW_{MO}} \times \frac{W_{MO}}{W_{MN}} \times 100 \quad (2)$$

Where MW_{MO} and W_{MO} are molecular weight and weight of manganese oxide respectively.

2.3 Manganese Oxide Characterisation

With XRD (Bruker) operating at 40mA and 40kV, using Cu-K radiation and a nickel filter, the resulting manganese oxide powder was characterised in the 2θ range from 5 to 80 degrees in increments of 0.02 degrees, at a rate of 1sec/ step. The morphology was observed using SEM running at 15kV.

Copper ions concentration was found using Atomic Absorption Spectroscopy (AAS) (GBC-932) at 249.2nm during the adsorption procedure.

2.4 Experiments

At room temperature, batch adsorption studies were conducted to examine the impact of various factors, including the effect of pH (varied between 2 to 5); effect of contact time (varied between 10 to180 minutes); effect of MnO_2 dosage (varied between 2 to 20g/L); effect of copper concentration (varied from 100 to 500mg/L) affecting the copper adsorption process. Unless otherwise specified, the adsorption conditions were as follows: Initial copper ion concentration 500mg/L, MnO_2 dosage 2g/L, contact time 180 min, pH of solution 5.0.

The experimental procedure was as follows: A series of reagent bottles containing 50mL copper solution, each of known initial concentration was taken. To this, a known amount of adsorbent was added and stirred at a speed of 120rpm. After the successful completion of each run, the contents from the reagent bottle were filtered and the filtrate was centrifuged. The supernatant liquid was analysed for final copper concentration using AAS. Copper uptake (Equation 3) and the percentage removal of copper (Equation 4) were calculated as follows:

$$q = \frac{C_I - C_F}{m} \quad (3)$$

$$\%R = \frac{C_I - C_F}{C_I} \quad (4)$$

q is the weight of copper adsorbed/ g of MnO_2; C_I and C_F are copper concentration at initial and adsorption time (mg/L); m is the MnO_2 dosage (g/L); $\%R$ is the percentage removal of copper.

3.0 Results and Discussion

3.1 Material Characterisation

The synthesized MnO_2 powder's morphological structure was examined by SEM imaging depicted in Figure 1. The structure is highly porous hence providing more surface area for adsorption. XRD analysis was done to investigate the crystallinity, crystallite size and identification of the MnO_2 product. Figure 2 shows the XRD pattern. The MnO_2 XRD pattern and the results for crystalline MnO_2 as seen in other investigations were found to be similar[8-10]. Using Equation

5, Scherrer's formula was used to determine the mean crystallite size of MnO_2, which was found to be 36nm[11].

$$D = \frac{0.94\lambda}{\beta Cos\theta} \quad (5)$$

D = size of the MnO_2 crystallite, λ = wavelength of the radiation, β= bandwidth at half height, θ= diffraction peak angle.

3.2 Influence of Initial pH

The effect of initial pH on copper removal was studied at 1000 mg/L copper concentration with pH 2 to 5 as shown in Figure 3. Removal efficiency enhanced from 7.73% to 26.57% with an increase in pH from 2 to 5. Lower copper removal at lower pH could be attributed to the protons competing with copper ions for the active sites on the selected adsorbent. Metal hydroxide formation was observed above pH 5. Similar behaviour was reported in the literature[12,13].

3.3 Influence of Time

The influence of contact time was studied as shown in Figure 4. The first 10 minutes represented a rapid phase owing to the high available surface area for adsorption; followed by a slow phase which eventually reached equilibrium. The adsorption process took 180 minutes to reach equilibrium and hence was considered to be the optimum time for this study.

3.4 Influence of MnO_2 Dosage

The amount of MnO_2 added was varied from 2g/L to 20g/L as shown in Figure 5. From the results, it was found that as the adsorbent dosage increased, the overall adsorption increased, but the metal uptake gradually reduced. This was due to increased active sites for fixed metal ion concentration[14]. MnO_2 dosage of 10g/L offered nearly 80% copper removal. However, it was also noteworthy that a dosage of 15g/L reduced copper ions to non-detectable levels.

3.5 Influence of Initial Copper Ion Concentration

To study the influence of initial copper ion concentration, synthetic solutions of copper ranging from 100 to 500mg/L were taken for the batch experiments. The result as shown in Figure 6 showed that as the copper concentration increased, the percentage adsorption

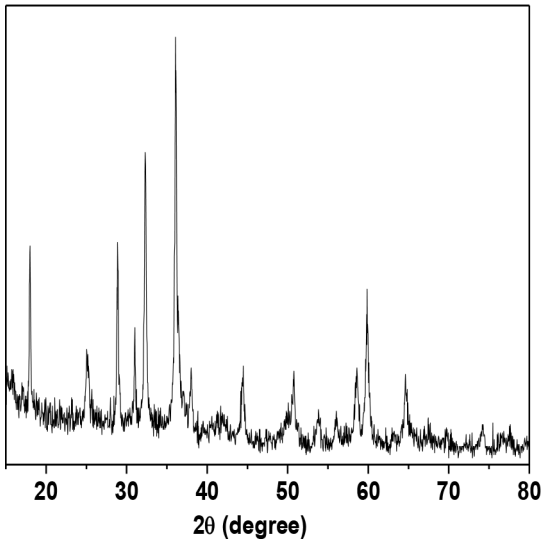


Figure 2. XRD image of synthesized nano powder.

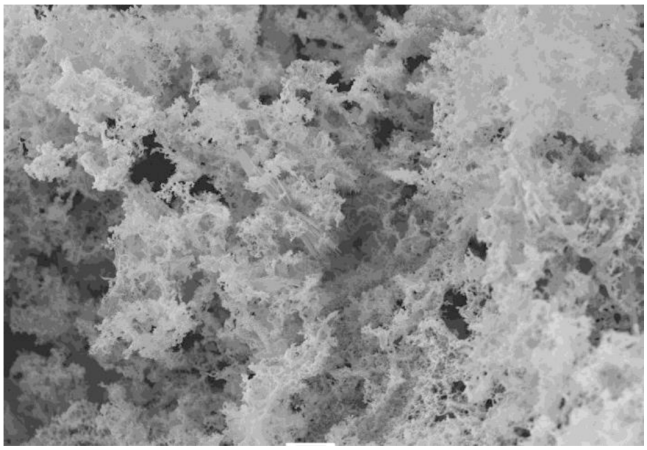


Figure 1. Scanning Electron Microscope image at 1000X magnification.

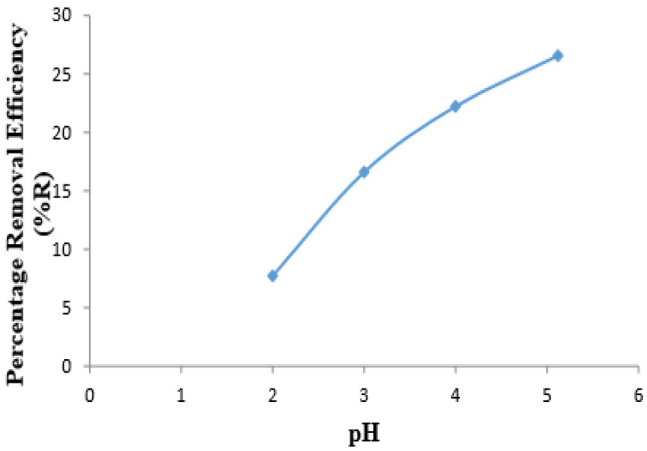


Figure 3. Influence of initial pH on copper removal efficiency.

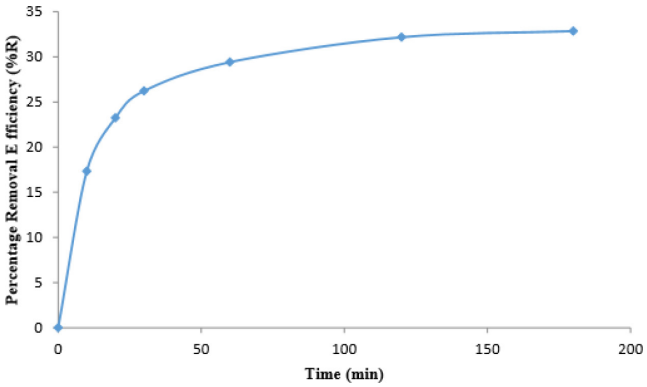


Figure 4. Influence of contact time on copper removal efficiency.

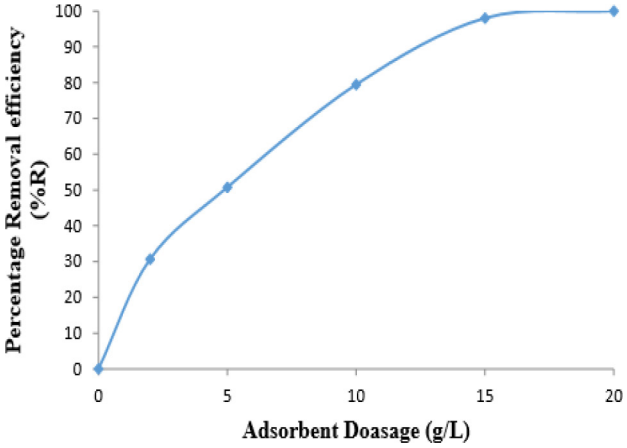


Figure 5. Influence of adsorbent dosage on copper removal efficiency.

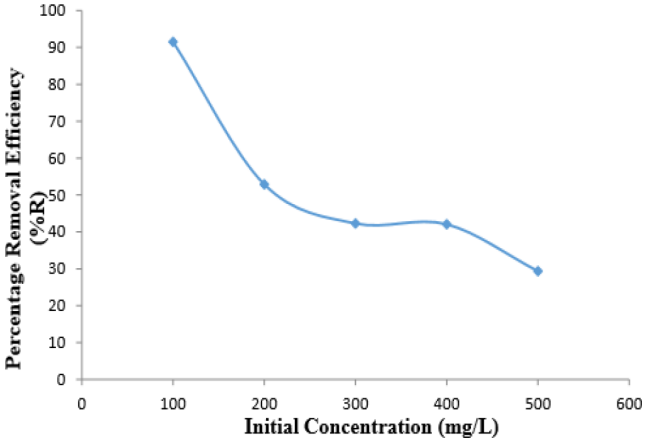


Figure 6. Influence of initial copper ion concentration on percentage removal.

decreased. This decrease could be due to the saturation of active sites in the adsorbent. The metal uptake increased due to the availability of more ions in the solution for adsorption.

3.6 Adsorption Isotherms and Kinetic Models

The two adsorption isotherm models were tested to fit the contact time data. The findings indicated adsorption followed Langmuir isotherm with a high regression coefficient of 0.9632. The correlation coefficient of the Freundlich isotherm model was 0.7395. The Langmuir isotherm constants were also calculated and found to be q_m

Table 1. Comparison with various adsorbents.

Sl no	Adsorbent	Dosage g/L	pH	Contact time min	C_i mg/L	q_{max} mg/g	Reference
1	Sulfonated magnetic graphene oxide composite	1	4.68	360	73.71	62.73	[17]
2	Tea residue	0.4	5	100	0.5	60.827	[18]
3	Saw dust	40	4	120	92	3.6	[19]
4	Activated carbon (Phaseolus aureus hulls)	1	7	60	100	19.5	[20]
5	Activated carbon (Ceiba pentandra hulls)	10	6	120	80	20.78	[21]
6	Modified fly ash	-	6.4	120	6.5	21.50	[22]
7	Sulfonated magnetic graphene oxide composite	40	4.68	360	73.71	62.73	[23]
8	Agricultural waste sugar beet pulp	1	4	180	250	28.5	[24]
9	Activated carbon from a precursor hazelnut husks	0.12	5.7	60	200	6.645	[25]
10	Amino-functionalized magnetic nano adsorbent	0.1	6	5	10	25.77	[26]
11	Manganese oxide nano powder	15	5	180	500	83.33	this study

=80 mg/g and K_L=0.04275 L/mg. The application of Ho's pseudo-second-order model to the adsorption of copper ions to the experimental data converged well. The pseudo-second-order rate constant was 0.001846 g/mg-min, the q_e calculated was 83.33 mg/g and the regression coefficient was 0.9935. Lagergren's pseudo-first-order kinetic model[15,16] yielded a fairly acceptable regression coefficient of 0.9648[17]. Table 1 gives a comparison of copper uptake values of different adsorbents with the present study. Prepared MnO_2 nano powder exhibited higher copper removal potential.

4.0 Conclusions

Manganese oxide nanopowder was synthesised using the combustion process. It was characterised using SEM and XRD. The mean crystallite size was found to be 36nm. Batch experiments were conducted to study the adsorption of copper ions using synthesised nanopowder. Several variables that may influence the adsorption process, such as pH, contact duration, initial metal ion concentration and MnO_2 dose are studied. It was found that with an initial copper ion concentration of 500 mg/L, MnO_2 dosage of 15 g/L, pH of 5.0 and a contact time of 180 minutes, the final copper concentration was reduced to non-detectable levels.

The study also showed that the adsorption followed Langmuir adsorption isotherm and Ho's pseudo-second-order kinetic model which implied a monolayer chemisorption process. The MnO_2 nanopowder exhibited a tremendous adsorption ability to remove copper from mining wastewater.

5.0 Acknowledgements

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6.0 References

1. Ngah WW, Kamari A, Koay YJ. Equilibrium and kinetics studies of adsorption of copper (II) on chitosan and chitosan/PVA beads. Int J Biol Micromol. 2004; 34(3):155-161. https://doi.org/10.1016/j.ijbiomac.2004.03.001 PMid:15225987.
2. Ngah WW, Hanafiah MM. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. Bioresour Technol. 2008; 99(10):3935-3948. https://doi.org/10.1016/j.biortech.2007.06.011 PMid:17681755.
3. Özer A, Özer D, Özer A. The adsorption of copper (II) ions on to dehydrated wheat bran (DWB): Determination of the equilibrium and thermodynamic parameters. Process Biochem. 2004; 39(12):2183-2191. https://doi.org/10.1016/j.procbio.2003.11.008
4. Chen Z, Meng H, Xing G, Chen C, Zhao Y, Jia G, Wang T, Yuan H, Ye C, Zhao F, Chai Z. Acute toxicological effects of copper nanoparticles *in vivo*. Toxicol Lett. 2006; 163(2):109-120. https://doi.org/10.1016/j.toxlet.2005.10.003 PMid:16289865.
5. Patil KC, Aruna ST, Mimani T. Combustion synthesis: An update. Curr Opin Solid State Mater Sci. 2002; 6(6):507-512. https://doi.org/10.1016/S1359-0286(02)00123-7
6. Patil KC, Aruna ST, Ekambaram S. Combustion synthesis. 1997; 2(2):158-165. https://doi.org/10.1016/S1359-0286(97)80060-5
7. Kingsley JJ, Patil KC. A novel combustion process for the synthesis of fine particle α-alumina and related oxide materials. Mater Lett. 1988; 6(11-12):427-432. https://doi.org/10.1016/0167-577X(88)90045-6
8. Salam MA. Synthesis and characterization of novel manganese oxide nanocorals and their application for the removal of methylene blue from aqueous solution. Chem Eng J. 2015; 270:50-57. https://doi.org/10.1016/j.cej.2015.02.022
9. Qusti AH. Removal of chromium (VI) from aqueous solution using manganese oxide nanofibers. Journal of Industrial and Engineering Chemistry. 2014; 20(5):3394-3399. https://doi.org/10.1016/j.jiec.2013.12.025
10. Zhang L, Tian Y, Guo Y, Gao H, Li H, Yan S. Introduction of α-MnO_2 nanosheets to NH_2 graphene to remove Cr^{6+} from aqueous solutions. RSC Adv. 2015; 5(55):44096-44106. https://doi.org/10.1039/C5RA04545B
11. Ahmad T, Ramanujachary KV, Lofland SE, Ganguli AK. Nanorods of manganese oxalate: a single source precursor to different manganese oxide nanoparticles (MnO, Mn_2O_3, Mn_3O_4). J Mater Chem A. 2004; 14(23):3406-3410. https://doi.org/10.1039/b409010a
12. Chen YH, Chen YD. Kinetic study of Cu (II) adsorption on nanosized $BaTiO_3$ and $SrTiO_3$ photocatalysts. J Hazard Mater. 2011; 185(1):168-173. https://doi.org/10.1016/j.jhazmat.2010.09.014 PMid:20888690.
13. Roy A, Bhattacharya J. Removal of Cu (II), Zn (II) and Pb (II) from water using microwave-assisted synthesized maghemite nanotubes. Chem Eng J. 2012; 211:493-500. https://doi.org/10.1016/j.cej.2012.09.097
14. Kulkarni RM, Shetty KV, Srinikethan G. Cadmium (II) and nickel (II) biosorption by *Bacillus laterosporus* (MTCC 1628). J Taiwan Inst Chem Eng. 2014; 45(4):1628-1635. https://doi.org/10.1016/j.jtice.2013.11.006
15. Lagergren SK. About the theory of so-called adsorption of soluble substances. Sven. Vetenskapsakad. Handingarl. 1898; 24:1-39.

16. Ho YS. Review of second-order models for adsorption systems. J Hazard Mater. 2006; 136(3):681-689. https://doi.org/10.1016/j.jhazmat.2005.12.043 PMid:16460877.
17. Hu XJ, Liu YG, Wang H, Chen AW, Zeng GM, Liu SM, Guo YM, Hu X, Li TT, Wang YQ, Zhou L. Removal of Cu (II) ions from aqueous solution using sulfonated magnetic graphene oxide composite. Sep Purif Technol. 2013; 108:189-95. https://doi.org/10.1016/j.seppur.2013.02.011
18. Dizadji N, Anaraki NA. Adsorption of chromium and copper in aqueous solutions using tea residue. Int J Environ Sci Technol. 2011; 8:631-638. https://doi.org/10.1007/BF03326248
19. Argun ME, Dursun S, Ozdemir C, Karatas M. Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. J Hazard Mater. 2007; 141(1):77-85. https://doi.org/10.1016/j.jhazmat.2006.06.095 PMid:16879919.
20. Rao MM, Ramana DK, Seshaiah K, Wang MC, Chien SC. Removal of some metal ions by activated carbon prepared from Phaseolus aureus hulls. J Hazard Mater. 2009; 166(2-3):1006-1013. https://doi.org/10.1016/j.jhazmat.2008.12.002 PMid:19135782.
21. Rao MM, Ramesh A, Rao GP, Seshaiah K. Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls. J Hazard Mater. 2006; 129(1-3):123-9. https://doi.org/10.1016/j.jhazmat.2005.08.018 PMid:16191464.
22. Alinnor IJ. Adsorption of heavy metal ions from aqueous solution by fly ash. Fuel. 2007; 86(5-6):853-7. https://doi.org/10.1016/j.fuel.2006.08.019
23. Hu XJ, Liu YG, Wang H, Chen AW, Zeng GM, Liu SM, Guo YM, Hu X, Li TT, Wang YQ, Zhou L. Removal of Cu (II) ions from aqueous solution using sulfonated magnetic graphene oxide composite. Sep Purif Technol. 2013; 108:189-95. https://doi.org/10.1016/j.seppur.2013.02.011
24. Aksu Z, İşoğlu İA. Removal of copper (II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp. Process Biochem. 2005; 40(9):3031-3044. https://doi.org/10.1016/j.procbio.2005.02.004
25. Imamoglu M, Tekir O. Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks. Desalination. 2008; 228(1-3):108-113. https://doi.org/10.1016/j.desal.2007.08.011
26. Hao YM, Man C, Hu ZB. Effective removal of Cu (II) ions from aqueous solution by amino-functionalized magnetic nanoparticles. J Hazard Mater. 2010; 184(1-3):392-399. https://doi.org/10.1016/j.jhazmat.2010.08.048 PMid:20837378.