

Sorption characteristics of aqueous copper onto residue generated in ammoniacal leaching of manganese nodules

N. S. Randhawa^{1*}, R. K. Jana¹ and N. N. Das²

¹Metal Extraction & Forming Division, CSIR-National Metallurgical Laboratory, Jamsshedpur – 831 007

²PG Department of Chemistry, North Orissa University, Baripada – 757 003

Abstract

The present paper reports the studies on copper removal from its aqueous solution using residue generated in the process of reduction roast- ammonia leaching of manganese nodules. The leached residue was washed with water to remove the entrapped liquor containing metals from leaching operation, dried and used for adsorption of aqueous Cu(II) under varying experimental conditions. The particle size analyses of manganese nodule residue (*w*MNR) showed very fine particles with mean diameters (d_{50}) of 17.8 μm . The BET surface area of *w*MNR was found to be 66.7 m^2g^{-1} . Adsorption studies of copper aqueous solution by batch equilibrium method indicated that the equilibrium was attained within 4 h. The percentage of Cu(II) adsorption increased with increase of leached residue dose but decreased with increase of initial Cu(II) concentrations. The adsorption was found to be dependent on initial pH of Cu(II) solution, which increased with increase in initial pH. During uptake of Cu(II), various metal ions, especially Mn and Fe, were found to be released from leached residue, which decreased with increase of pH. Pseudo second-order kinetics was applicable for the Cu(II) adsorption. Adsorption data were satisfactorily fitted to the Langmuir isotherms. The maximum adsorption capacity determined by Langmuir isotherm was found to be 26.95 mg g^{-1} at pH 5.5 and 303 K. Thus the leach residue found to be useful for removal of heavy metal like copper from the industrial effluent.

Keyword: Leach residue; Adsorption; Copper; Kinetics; Isotherm

1. Introduction

Effluents from most of the industrial units contain metallic pollutants. Heavy metals present in these effluents, when discharged untreated, pollute water bodies and pose threat to ecosystem. Heavy metals are non-biodegradable and tend to accumulate in living organisms, causing various life threatening disorders [1]. Copper is major pollutant in the effluents discharged from industries working in the field of electroplating, electrical & electronic, hydrometallurgical processing, ore beneficiation, tanneries etc.[2]

In India, the permissible limit for discharge of copper into inland surface waters and public sewers are 3.0 mg L^{-1} [3] and for drinking water is 0.05 mg L^{-1} [4]. The important technologies available for cadmium removal are chemical precipitation,

electrocaugulation, electro flotation, ion exchange, reverse osmosis and adsorption onto activated carbon [5]. Among them, adsorption technique has been viewed as most attractive due to factors like simple operation and effectiveness. Moreover, many adsorption techniques regenerate the adsorbent and reduce the operational cost. The key factor for the selection of an adsorbent lies with its effectiveness and most importantly its cost. Apart from much studied adsorbents like activated carbon, non-conventional and minerals based adsorbents including agricultural wastes, calcite, biomass, red-mud, silica gel and blast furnace sludge [6-9] have also been tried for the removal of Cu(II) from waste water. Oxides have been widely discussed for metals removal from aqueous solutions [10]. They have been shown to remove metals to trace concentrations and the adsorbed metals could be recovered and reused.

The present study aimed at utilization of residue generated during the processing of manganese nodules for the recovery of valuable metals by reduction roasting–ammoniacal leaching at CSIR-National Metallurgical Laboratory (CSIR-NML), Jamshedpur, India [11]. Various parameter like pH of medium, initial Cu(II) concentrations, residue dose etc were investigated to ascertain the suitability of leach manganese nodule residue for Cu(II) removal from aqueous solution.

2. Materials and methods

2.1 Materials

The adsorbent material i.e. leached manganese nodule residue was obtained from large scale ammoniacal leaching of manganese nodules at NML. The leached residue was washed with water to remove the entrapped leach liquor and metal-amine complexes. The washed manganese nodule residue (*w*MNR) was dried in an oven at 110°C till the weight of dried residue became constant. Dried *w*MNR was stored in a desiccator to avoid moisture uptake. The synthetic stock solution (1000 mg L⁻¹) was prepared by dissolving AR grade Cu(NO₃)₂ (Merck) in distilled water. Solutions of 0.1M HNO₃ and 0.1M NaOH were used for pH adjustment. 0.1N KNO₃ was used to maintain the ionic strength in the adsorption experiments.

2.2 Methods

2.2.1 Sample characterization

The chemical composition of *w*MNR was determined by combination of standard wet chemical and instrumental methods. Phases present in residue were identified by XRD

recorded (2° min^{-1}) in Siemens D 500 X-ray diffractometer using CuK_α radiation. Size analysis was carried out in Malvern Mastersizer after ultrasonic liberation of particles. Surface area of the residue was measured by N_2 adsorption at 78K using a Quantachrome 4000E surface area analyser (Nova Instruments, USA).

2.2.2 Adsorption experiments

Adsorption of copper on $w\text{MNR}$ was carried by batch equilibrium method at constant temperature ($30 \pm 0.5^\circ\text{C}$) and stirring speed ($120 \text{ strokes min}^{-1}$). 50 mL of Cu(II) solution at desired concentration with appropriate amount of adsorbent in 100 mL stoppered conical flask was adjusted to required pH and the flask was mechanically shaken to attain the equilibrium. At equilibrium, the solid adsorbent was separated by filtration and remaining copper in the solution was analyzed by atomic absorption spectrometer (PerkinElmer AA400 analyst) after suitable dilution with distilled water. The effect of various parameters, such as contact time, pH of the adsorbate solution, initial copper concentration and the adsorbent dose were also studied.

3. Results & discussions

3.1 Adsorbent characterization

The chemical composition of major constituents of $w\text{MNR}$ is as follows: Fe, 10.19; SiO_2 , 16.44; Mn, 26.11; CaO, 0.36; MgO, 4.4 and Al_2O_3 , 3.54 %; loss on ignition, 17.01%. The pH_{zpc}, specific gravity, surface area of $w\text{MNR}$ are found to be 6.5, 3.1 and $66.7 \text{ m}^2\text{g}^{-1}$, respectively.

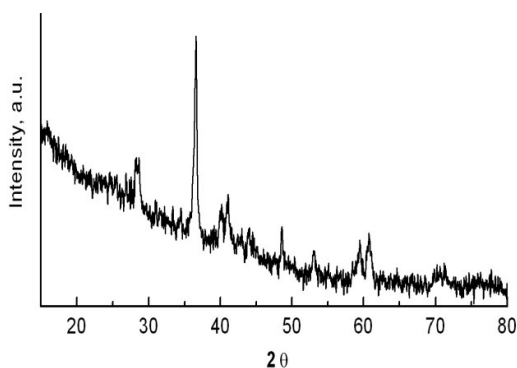


Fig 1 X-ray diffraction patterns of WMNR using CuK_α

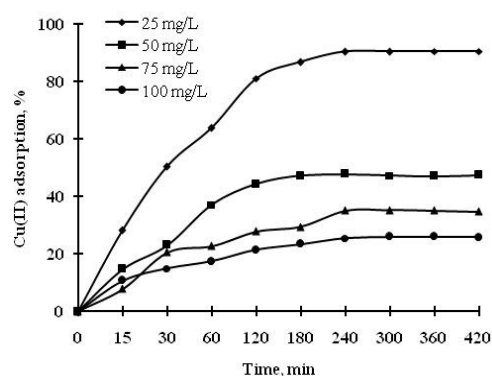


Fig 2 Effect of contact time on adsorption of Cu(II) at 303 K: $w\text{MNR}$ dose 1 gL^{-1} ; pH 5.5

The XRD pattern of air dried $w\text{MNR}$ shown in Fig. 1 exhibits a few low intensity peaks attributing mainly to MnCO_3 and manganese silicate phases. However, peaks of iron

oxide or manganese oxide were not observed due to their poor crystallinity/amorphous nature of samples. The size analysis indicated the high degree of fineness of the washed residue with d_{90} of 62.37 μm and d_{50} of 11.38 μm .

3.2 Kinetic study

3.2.1 Effect of time and initial concentration on adsorption

The time course of adsorption of Cu(II) on *w*MNR at varying initial concentrations is given in Fig. 2. It is apparent that Cu adsorption on *w*MNR attain the equilibrium after about 240 min. The Cu removal at equilibrium is 90, 48, 35 and 26 % for 25, 50, 75 and 100 mgL^{-1} initial Cu, respectively. Hence all further experiments were carried out with an equilibrium time of 240 min. Although the percentage of Cu adsorption decreases with increase of its initial concentration, the overall uptake increases progressively. For a fixed dose of adsorbent the decrease of Cu adsorption is primarily due to availability of limited number of site for adsorption.

3.2.2 Adsorption kinetics

Kinetics and the equilibrium of adsorption are the two important factors for the evaluation of the adsorption parameter. Kinetic studies were done at three temperatures (303, 313 and 323 K) with initial Cu concentration of 50 mgL^{-1} . It can be seen from Table 1 that the fitness of time course adsorption data into a pseudo second-order model [12] ($R^2 = 0.996, 0.999 \text{ \& } 0.999$) is relatively better than that for pseudo first-order kinetic models [13] ($R^2 = 0.994, 0.997 \text{ \& } 0.994$). The kinetics of Cu adsorption improved with temperature as indicated by increasing value of rate constant (k_2) and initial rate of adsorption (h).

Table 1 Pseudo first-order and pseudo second-order rate constants for Cu(II) adsorption on *w*MNR

Temp, K	Lagergren constants			Pseudo second order rate constants			
	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{ min}$)	R^2	q_e (mg g^{-1})	h ($\text{mg g}^{-1} \text{ min}$)
303	0.023	0.994	23.15	0.0011	0.996	27.78	0.874891
313	0.028	0.997	25.45	0.0020	0.999	33.33	2.192982
323	0.045	0.994	29.14	0.0032	0.999	38.46	4.739336

The effect of temperature on adsorption of Cu^{2+} on *w*MNR was further evaluated using Arrhenius equation. A plot of $\ln k_2$ versus $1/T$ yields a straight line, with slope $-E_a/R$. The

magnitude of the activation energy is commonly used as the basis for differentiating between physical and chemical adsorption. The activation energy for Cu(II) adsorption onto wMNR was ranged between 40-50 kJ mol⁻¹ for different initial concentrations, suggesting that the Cu(II) ions was chemically adsorbed onto the WMNR surface.

3.3 Equilibrium study

3.2.1 Effect of wMNR dose on Cu adsorption

Adsorption of Cu with varying adsorbent dose, carried out to assess the effect of amount of adsorbent on Cu removal, is presented in Fig. 3. The results show that the equilibrium concentration (*C_e*) of Cu decreases with increase in the weight of wMNR, which is 40 mgL⁻¹ for 0.25 gL⁻¹ of wMNR but only 0.2 mgL⁻¹ for 5.0 gL⁻¹ of WMNR is observed. Increase of wMNR dose provides higher surface area and active sites for adsorption of Cu and ultimately responsible for more uptake of Cu.

3.2.2 Effect of pH on adsorption

The solution pH is another important parameter which affects adsorption of heavy metal ions. The adsorption of copper was studied over the range of pH ~ 3–8 and the results are shown in Fig. 4. It is seen the adsorption of Cu increase with increase of pH.

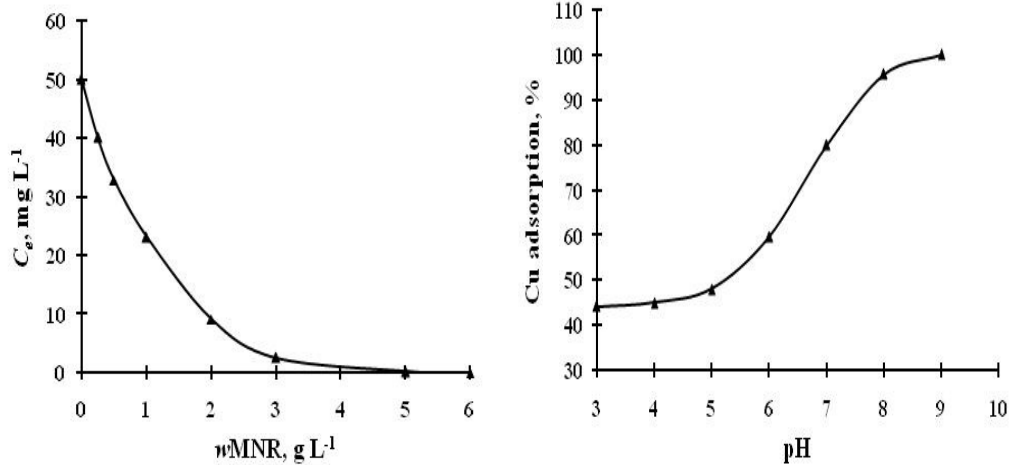


Fig 3 Effect of weight of wMNR on Cu (50 mgL⁻¹) adsorption at 303 K and pH 5.5 Fig 4 Effect of pH on Cu (50 mgL⁻¹) adsorption at 303K with wMNR dose: 1.0 g L⁻¹

The increase may be partly attributed to the formation of different hydroxo species with rise in solution pH. Based on the hydrolysis constants [14-15] of different metal ions as defined in Eq. 1.



The Cu(II) speciation diagram [16] shows that the dominant Cu(II) species up to pH 6.0 is Cu^{2+} . The $\text{Cu}(\text{OH})^+$ is 40% present in pH range pH 6-8 whereas dominating Cu(II) species at pH >8.0 is $\text{Cu}(\text{OH})_2$, therefore at lower pH there is a competition effect between the H_3O^+ ions and Cu(II) ions. At low pH values, the concentration of H_3O^+ far exceeds that of Cu(II) ions and hence, these ions occupy the surface binding sites, leaving Cu(II) ions free in solution. As the pH value increase, the competing effect of H_3O^+ ions decreased and the positively charged Cu^{2+} and $\text{Cu}(\text{OH})^+$ ions hook up the free binding sites. Hence, the metal uptake is increased on the surface of the adsorbent with the increase in pH.

The other important factor, which might contribute to the higher adsorption of metal ions with increased pH, is the pH_{pzc} of wMNR. At any pH below pH_{pzc} , the surface of metal oxides/ oxyhydroxides is positively charged and at pH above pH_{pzc} , the surface is negative [17]. When the solution pH exceeded pH_{pzc} , the metal species are more easily attracted by the negatively charged surface of adsorbent, favouring accumulation of metal species on the surface and thus promoting adsorption.

3.2.3 Adsorption isotherm studies

The equilibrium adsorption data were fitted the linearised form of Langmuir (Eq. 2) and Freundlich (Eq. 3) models [19,20]:

$$\frac{C_e}{q_e} = \frac{1}{bQ^o} + \frac{C_e}{Q^o} \quad \dots\dots\dots 2$$

$$\ln q_e = \ln K_f + n \ln C_e \quad \dots\dots\dots 3$$

where, C_e is equilibrium concentration (mg L^{-1}); q_e is amount adsorbed at equilibrium (mg g^{-1}); K_f , b , n are isotherm constants and Q^o is adsorption maxima or adsorption capacity (mg g^{-1}).

The isotherm studies were carried out with the Cu(II) concentration between 5-100 mg L^{-1} , pH 5.5 and wMNR dose of 1 g L^{-1} . The calculated parameter from Langmuir plot of C_e versus C_e/q_e and Freundlich plot of $\ln q_e$ versus $\ln C_e$ are given in Table 2. It is evident that the adsorption of Cu(II) fits better with the Langmuir model ($R^2= 0.999$ at all three temperatures) as compared to the Freundlich model ($R^2= 0.914, 0.939$ & 0.985 at 303, 313 & 323 K respectively) for the concentration range under consideration. This indicates that the adsorption of Cu(II) follows Langmuir model yielding better linearity.

Increasing maximum loading of Cu(II) onto wMNR with temperature indicates endothermic nature of adsorption reaction.

Table 2 Langmuir and Freundlich isotherm parameters

Temp, K	Langmuir isotherm			Freundlich isotherm		
	Q_o	K_a	R^2	K_f	1/n	R^2
303	26.95	1.28	0.999	12.42	0.21	0.914
313	32.36	2.41	0.999	14.93	0.22	0.939
323	40.32	2.82	0.999	20.04	0.16	0.985

To determine whether the adsorption process was favorable or unfavorable, the value of R_L constant is calculated. R_L is a dimensionless constant separation factor [21] where $R_L > 1$ unfavorable; $R_L = 1$ linear; $0 < R_L < 1$ favourable; $R_L = 0$ irreversible. The value of R_L was calculated from the Eq. 4.

$$R_L = 1 / (1 + bC^o) \quad \dots\dots\dots 4$$

Where C^o is the initial metal concentration (mgL^{-1}) and b is the Langmuir parameter i.e. energy of interaction at the surface. The calculated values of R_L are in the range 0.135-0.004, suggesting the adsorption process is favorable for Cu(II) on wMNR.

4. Conclusions

The following conclusions were drawn from the adsorption studies:

1. The leached manganese nodule residue generated by reduction roast-ammonia leaching has been shown to be a potentially useful material for removal of aqueous copper.
2. The uptake of Cu increases with increasing its initial concentrations and equilibrium was attained in 240 min time irrespective of initial concentration.
3. The regression coefficient value showed that the adsorption of Cu on leached manganese nodule residue followed pseudo second-order kinetics.
4. The Q^o i.e. maximum loading capacity value for Cu adsorption on this adsorbent was found to be 26.95 mg g^{-1} at pH 5.5 and 303 K.
5. The adsorption data well fitted to the Langmuir isotherm. The separation (R_L) value calculated from isotherm data depicted favorable adsorption of copper.

6. The value of kinetic rate constants and loading capacity of wMNR increased with increasing temperature indicated endothermic nature of adsorption reactions.
7. The values of activation energy indicated chemisorption type reaction in Cu(II) adsorption onto wMNR.

Thus adsorption properties of leached manganese nodule residue can be utilized for treatment of industrial effluents to bring down the high Cu metal for its safe disposal in inland water bodies.

5. Acknowledgement

The authors are thankful to Director, CSIR-NML, Jamshedpur for giving permission for presenting the paper.

6. References

- [1] Hanaa M., Eweida S., Eweida A., and Farag A., 2000, Heavy metals in drinking water and their environmental impact on human health, In: ICEHM2000, Cairo University, Egypt, pp. 542-556
- [2] Rozada, F., Otero, M., Moran, A. and García, A.I., 2008, Adsorption of heavy metals onto waste sludge-derived materials, *Bioresour. Technol.* 99, pp. 6332–6338.
- [3] ISI, Tolerance Limits for Industrial Effluents: ISI 2490, Part I. Indian Standard Institutions, 1982.
- [4] ISI, Drinking Water Specifications, IS 10500, 1991
- [5] Dermentzis, K., Davidis, A., Papadopoulou, D., Christoforidis, A. and Ouzounis, K., 2009, Copper removal from industrial wastewaters by means of electrostatic shielding driven electrodeionization, *Journal of Engineering Science and Technology Review* 2 (1), pp. 131-136
- [6] Bertocchi A. F, Marcello G., Roberto P. and Antonio Z., 2006, Red mud and fly ash for remediation of mine sites contaminated with As, Cd, Cu, Pb and Zn, *Journal of Hazardous Materials*, B134, pp. 112–119.
- [7] Filho N. L. D., Gushiken Y., Polito W. L. and Moreiza J. C., 1995, Sorption And preconcentrations of metalions in ethanol solutions with silica gel modified with benzinimidazole, *Talanta*, 42, pp. 1630-1663.
- [8] Degodo A.L., Perez C. and Copez F.A., 1998, Sorption of heavy metals on blast furnace sludge, *Indian Journal of Chem. Technol.*, 32, pp. 1989-1996.
- [9] Chhotu D. Jadia and M. H. Fulekar, 2009, Phytoremediation of heavy metals: Recent techniques, *African Journal of Biotechnology*, 8 (6), pp. 921-928.
- [10] Machida M., Yamazaki R., Aikawa M. and Tatsumoto H., 2005, Role of minerals in carbonaceous adsorbents for removal of Pb(II) ions from aqueous solution, *Separation and Purification Technology*, 46, pp. 88–94
- [11] Jana R. K., Pandey B. D. and Premchand, 1999, Ammoniacal leaching of roast reduced deep-sea manganese nodules, *Hydrometallurgy*, 53, pp. 45-56

- [12] Ho Y. S. and McKay G., 2000, The kinetic of sorption of divalent metal ion onto sphagnum moss peat, *Water Res.* 34, pp. 735–742.
- [13] Lagergren, S., Svenka, K., 1998, About the theory of so-called adsorption of soluble substances. *Vetenskapsakad Handl.* **24**(2), pp. 1–39
- [14] Perin D. D. and Dempsy B., 1974, Buffers for pH and Metal ion Control, Chapman & Hall, London, P. 104
- [15] Martell A. E. and Smith R. M., 1977, In: Critical Stability Constants (Inorganic Chemistry), vol. IV, Plenum, NewYork, P. 6
- [16] Das N. N. and Jana R. K., 2006, Adsorption of some bivalent heavy metal ions from aqueous solutions by manganese nodule leached residues, *J. Colloid Interface Sci.*, 293, pp. 253-262
- [17] Hall K. R., Eagleton L. C., Acrivos A. and Vermeulen T., 1966, Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant pattern conditions, *Ind. Eng. Chem. Fundam.*, 5, pp. 212–223
- [19] I. Langmuir, 1916, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (11), pp. 2221–2295.
- [20] H.M.F. Freundlich, 1906, Over the adsorption in solution, *J. Phys. Chem.* 57, pp. 385–471
- [21] K.Y. Foo and B.H. Hameed, 2010, Insights into the modeling of adsorption isotherm systems, *Chemical Engineering Journal*, 156, pp. 2–10