



THE EFFECTIVE REMOVAL OF CU(II), CD(II) AND PB(II) IONS FROM AQUEOUS SOLUTION BY USING LOW COST INDUSTRIAL ADSORBENT LIKE CHINA CLAY

Radhey Shyam^{1*} and Surekha Kannaujia²

Associate Professor Department of Chemistry D B S (PG) College Dehradun 248 001 (UK) India.

***Corresponding Author: Radhey Shyam**

Associate Professor Department of Chemistry D B S (PG) College Dehradun 248 001 (UK) India.

Article Received on 26/07/2022

Article Revised on 16/08/2022

Article Accepted on 06/09/2022

ABSTRACT

In this paper, we take adsorbent, with low cost and high-efficiency adsorption of Cu(II), Cd(II) and Pb (II) from aqueous solution. For well-known adsorption of heavy metals by China clay, data were placed in the Langmuir and Freundlich isotherms models. Adsorption of heavy metals by China clay under the effect of pH, adsorbent dosage and concentration were studied. Langmuir isotherm shows better fit for heavy metals adsorption than the Freundlich isotherm. Under specified conditions, maximum single metal adsorption capacities of the China clay (q_{max}) for Cu(II), Cd(II) and Pb (II) were 77.76, 76.16 and 191.93 mg/g, under Langmuir model equations. Adsorption kinetic data fitted well with pseudo-second-order kinetic model ($R^2 \leq 0.9996, 0.9995$ and 0.9878) for Cu(II), Cd(II) and Pb (II) loaded on China clay.

KEYWORDS: Adsorption Isotherm, China Clay, Heavy metals etc.

INTRODUCTION

Water polluted by heavy metals is one of the major environmental problems, heavy metals enter the water ecosystem from many sources such as industries, manufacturing, printing processes, electroplating, textiles, metal products, and ceramics.^[1] Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. Wastewater containing heavy metals originated mainly from metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides galvanizing plants, stabilizers, thermoplastics, pigment manufacture etc. Permissible limit for copper in drinking water is 0.05 mg/L as per WHO norms and also 0.05 mg/L as per ISI prescribed limits, 1993. The maximum permissible value for Cadmium, according to German Law is 15 µg/L. The maximum permissible limit of Lead was 0.01 mg/l, reported in BIS and ISI standards. These metals are known to progressively accumulate in our ecosystem once they are introduced, from very low levels to levels that exceed the threshold in the environment. Heavy metal contamination of aquatic ecosystems poses a major health risk to humans and harms the ecosystem. As a result of their unstable nature and high toxicity, causing of cancer in organisms.^[2] Cadmium one of the most dangerous carcinogens for humans, can damage the kidneys and has negative health consequences on the lungs, cardiovascular system, and musculoskeletal system.^[3] For the removal of heavy metals from water, many technologies have been used recently such as Ion

exchange, adsorption techniques,^[4] filtration, precipitation,^[5] electrolysis, membrane separation, and active carbon adsorption.^[6] These methods have some drawbacks, such as expensive equipment, poor selectivity and incomplete technical. In recent years, many researchers around the globe have been studying adsorption method using industrial waste that can bind high concentrations of metals at a low cost and stable technology,^[7] adsorption is a widely accepted approach for removing heavy metals from aquatic environments which is both easy and effective.^[8] Adsorption is a viable choice because of its specific high surface area with low-cost, numerous surface functional groups. The use of industrial byproducts for removing metal from water has increased significantly in recent years.^[9-10] The main purpose of this research to eliminate heavy metals from water at single metal and mix metals condition. Find out changes in the adsorbent functions groups and surface pores/area after treatment, also investigate the best environment for heavy metals adsorption.

METHODOLOGY AND MATERIALS

Preparation and Chemical analysis of adsorbent

China clay is a mineral of kaolinite group. It does not swell with addition of water. The alumina content present in it does not form isomorphous series with any other metallic compounds. It is generally used in the manufacture of different types of ceramic goods. It has been used by several workers^[11-16] as an adsorbent for water and wastewater treatment by adsorption process. It was collected from Patharghatt village of Bhagalpur

district, Bihar (India).

Table 1: Chemical analysis of China clay as Adsorbent Constituents Percentage by weight.

SiO ₂	46.22
Al ₂ O ₃	38.40
CaO	0.86
Fe ₂ O ₃	0.68
MgO	0.37
Loss of ignition	13.47
Particle size	53 μm
Mean Particle size diameter	51×10 ⁻⁴ cm
Surface area	13.52 m ² g ⁻¹
Porosity	0.330
Density	2.692 gcm ⁻³

The Infra-red spectrum of adsorbent was recorded in KBr and nujol null using Perkin Elmer Spectrophotometer, Model 783 and 621 in the range of 4000-200 cm⁻¹.

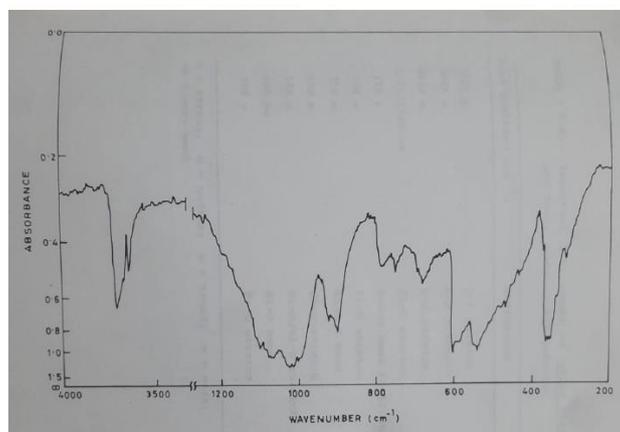


Figure 1: Infra red spectrum of china clay.

Adsorbent test

The adsorption investigation of Cu(II), Cd(II) and Pb (II) on adsorbent was conducted in 50ml metal ion solution in 100ml of the conical flask at 30°C by adding optimum adsorbent dosage shaken at 200 rpm for an hour. The effect of pH was investigated in the range of pH (3.0–9.0) by using a 1.5 g/L adsorbent and an initial concentration of 10 mg/L. The effect of time was investigated by increasing the adsorption period from (5 min- 1hour) by using a 1.5 g/L adsorbent and an initial concentration of 100 mg/L. The effect of adsorbent amount on Cu(II), Cd(II), and Pb (II) adsorption was examined by adsorbent increasing from 0.3 g/L to 3.0 g/L, the initial metal concentration of 100 mg/L at optimum pH of 6.6 and 7.0 for Cu(II), Cd(II), and Pb(II) ions, for 1 hour. The effect of initial metal concentration on adsorbent was examined by increasing metal concentration from 10 to 500 mg/L at optimum pH of 6.6 and 7.0 for Cu(II), Cd(II), and Pb(II) for 1 hour aim of the kinetic study was to find how long it takes to reach equilibrium using the 1.5 g/L amount of adsorbent. Isotherm was investigated using metal concentration from 10 to 500 mg/L by adding a 1.5 g/L amount of adsorbent. After adsorption process the solution was centrifuged at 4000 rpm for 15mins. The

adsorbent were isolated from the medium using filtration after equilibration and the filtrates were examined. The concentrations of Cu(II), Cd(II), and Pb (II) the filtrate was determined using atomic absorption spectroscopy.

The amount of metal ions adsorbed (qt) was calculated as the change in the aqueous phase concentration from initial value according to the equation,

$$qt = \left[\frac{C_0 - C_t}{m} \right] V \quad \dots\dots(1)$$

Where, C_0 and C_t (mg L⁻¹) are the initial metal ion concentration and at contact time t , V (L) is the volume of solution, and m (mg) is the amount of adsorbent added. The metal removal efficiency (percent metal removal) was calculated using the following equation^[17]:

$$\text{Percent metal removal (\% removal)} = \left[\frac{C_0 - C_e}{C_0} \right] 100 \quad \dots\dots(2)$$

RESULTS AND DISCUSSION

Effects of various factors

1. pH effect

pH is the most important factor of adsorption process,

which affects the adsorption of heavy metals by adsorbent.^[18] Due to competition between metal and H⁺ ions, the solution of pH impacts adsorption of metal ions at active sites of adsorbent. Adsorption of the metal ions on functional groups sites present on the outer surface of adsorbent depends on the pH of the solution. As a result, initial 3.0–9.0 pH values were used to test the influence of pH shown in Fig. 3. At pH 3, it was discovered that relatively little adsorption occurs. The adsorption capacity increased steadily in the pH range 3.0–6.0, with maximum removal recorded at pH 6.0 for Cu (II), Cd (II), and 7.0 for Pb (II). The poor metals adsorption at pH

3.0 can be explained by the protonation of active sites by H⁺ ions. The H⁺ ions on the adsorbent surface are attracted by electrostatic repulsion at low pH values, so they occupy a large portion of the adsorption sites, and less Cu (II), Cd (II), and Pb (II) can be adsorb. The rising in pH makes the surface charge of adsorbent more negatively charged, resulting in greater adsorption of Cu(II), Cd(II), and Pb (II) which reached equilibrium at pH 6.0, 6.0, and 7.0. Ion adsorption diminishes at higher pH (>7.0), which could be attributed to the development of soluble hydroxyl complexity of Cu(II), Cd(II), and Pb (II).

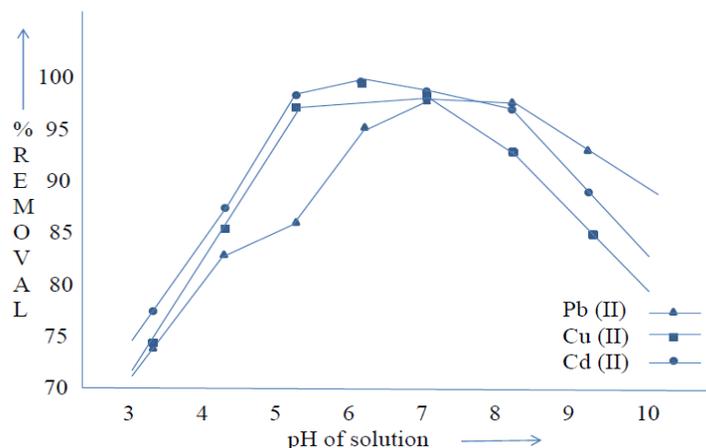


Figure 2: Effect of pH on the adsorption of Cu (II), Cd (II), and Pb (II) ions onto China Clay.

2. Dosage effect

The effect of adsorbent Dosage on adsorption process was done by increasing the adsorbent dosage from 0.3 to 3.0 g, the effect of adsorbent dosage on the elimination of heavy metal ions Cu (II), Cd (II) and Pb(II) as shown in Figure 3. Experiments demonstrated that as the adsorbent dosage is increased, the percentage of metal ions removed increases as well. The increased number of functional groups and convenient adsorption sites for metal ions was the cause of this rise [18]. The adsorption

process approaches equilibrium due to excessive congestion of adsorbent particles due to adsorption site overlap after a constant increase in the percentage of metal ions extracted from the aqueous solution. By increasing adsorbent dosage from 0.3 to 3.0 g the Cu (II) removing percentage was also increased from 94.0% to 99.1%, Cd (II) from 92% to 99.2% and Pb (II) removing percentage increased from 85.0% to 98.5%. We select the optimum adsorption dosage for rest of experiment 1.5 mg/L.

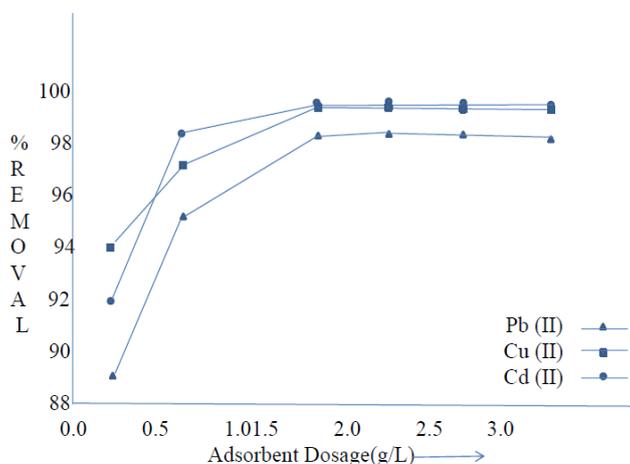


Figure 3: Effect of adsorbent dosage on the adsorption of Cu (II), Cd(II), and Pb (II) on adsorbent.

Adsorption isotherms

The equilibrium adsorption process in equilibrium can be

explained using Langmuir and Freundlich adsorption isotherms, The Langmuir isotherm is represented by the

following Equation:

$$q_e = q_{max} \cdot K_L \cdot C_e / (1 + K_L \cdot C_e) \quad \dots\dots\dots(3)$$

The linear form of the Langmuir equation is expressed as:

$$C_e/q_e = C_e/q_{max} + 1/K_L \cdot q_{max} \quad \dots\dots\dots(4)$$

Where, C_e is the adsorption concentration at equilibrium (mg/L), q_e is the amount of metal adsorb by adsorbent (mg/g), and q_{max} as the maximum monolayer coating capacity (mg/g). K_L is the Langmuir isotherm constant (L/mg). The Freundlich isotherm experimental equation is expressed by the following eq. (5):

$$\log q_e = \log k_f + (1/n) \log C_e \quad \dots\dots\dots(5)$$

Where, k_f represents the Freundlich isotherm constant (mg/g), n represents adsorption intensity, C_e represents the adsorbate concentration at equilibrium (mg/L), and q_e represents how much metal is adsorb by adsorbent (mg/g). The performance of adsorption test adsorbent is

affected by the initial concentrations of Cu(II), Cd(II) and Pb (II) Figure 4 represents finding binding affinity, adsorption capacity, and surface features of the adsorbent by using adsorption isotherm, all of which aid in understanding the adsorbate-adsorbent binding mechanism. The adsorption behavior of adsorbent for Cu(II), Cd(II) and Pb (II) an analysis of uptake was conducted using the Langmuir's and Freundlich's isotherms. Adsorbent surfaces have a finite number of adsorption sites in Langmuir's isotherm, where Freundlich's isotherm indicates adsorption occurs on a heterogeneous surface sorbent. Table: 2 shows, that the results of the Langmuir isotherm are the best fit because the value of the linear regression coefficient ($R^2 > 0.99$ for copper, cadmium ions and $R^2 > 0.98$ for lead ions) of Langmuir's isotherm was discovered to be higher than that of Freundlich's isotherm ($R^2 > 0.93$ for all cases). Table 2 it confirmed monolayer adsorption of Cu(II), Cd(II) and Pb (II) on China clay. For Cu, Cd and Pb the maximum adsorption capacity of China clay was found to be 77.76, 76.16 and 191.93 mg/g respectively.

Table 2: Isotherm parameters for the removal of Cu (II), Cd (II) and Pb (II) by China clay.

Isotherms	Parameters	Cu(II)	Cd(II)	Pb(II)
Freundlich	k_f	4.55	1.03	1.01
Freundlich	$1/n$	0.5311	0.3287	0.9548
Freundlich	R^2	0.9311	0.9986	0.9882
Langmuir	q_{max} (mg/g)	77.76	76.16	191.93
Langmuir	K_L (L/mg)	0.0306	0.0399	0.0054
Langmuir	RL	0.3949	0.3336	0.7856
Langmuir	R^2	0.9994	0.9986	0.9882

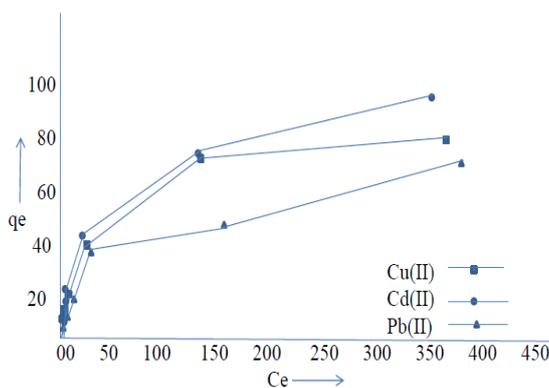


Figure 4: Effect of initial concentration on the adsorption of Cu (II), Cd (II) and Pb (II) on China clay.

CONCLUSION

In the present study heavy metals such as Cu (II), Cd (II) and Pb (II) were selected for removal from aqueous solutions using adsorption technique. A particle size of 53 μm was observed to be highly efficient for the removal of such metal ions. The present adsorbent China clay can be used as an industrial scale to remove Cu (II), Cd (II) and Pb (II) respectively. Hence, it is necessary to remove these metals from industrial effluents before discharging waste water into the environment. The data thus obtained may be helpful for designing and fabricating a treatment plant

for the removal of nickel present in wastewaters.

REFERENCES

1. Z. Aksu, I.A. Isoglu, Removal of copper (II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, *Process Biochem*, 2005; 40 (9): 3031–3044.
2. Labidi, A.M. Salaberria, S.C. Fernandes, J. Labidi, M. Abderrabba, Adsorption of copper on chitin-based materials: kinetic and thermodynamic studies, *J. Taiwan Inst. Chem. Eng*, 2016; 65: 140–148.

3. H. Li, J. Watson, Y. Zhang, H. Lu, Z. Liu, Environment-enhancing process for algal wastewater treatment, heavy metal control and hydrothermal biofuel production: a critical review, *Bioresour. Technol*, 2020; 298: 122421.
4. X. Yang, Y. Wan, Y. Zheng, F. He, Z. Yu, J. Huang, H. Wang, Y.S. Ok, Y. Jiang, B. Gao, Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: a critical review, *Chem. Eng. J*, 2019; 366: 608–621.
5. T. Ma, T. Nasser, A new simple method for the treatment of waste water containing Cu (II), Zn (II) Ions using adsorption on dried *Conocarpus erectus* leaves, *J. Basrah Res. (Sci.)*, 2013; 39 (2A).
6. W.S. Chai, J.Y. Cheun, P.S. Kumar, M. Mubashir, Z. Majeed, F. Banat, S.H. Ho, P.L. Show, A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application, *J. Clean. Prod*, 2021; 296: 126589.
7. D. Chen, Z. Zheng, K. Fu, Z. Zeng, J. Wang, M. Lu, Torrefaction of biomass stalk and its effect on the yield and quality of pyrolysis products, *Fuel*, 2015; 159: 27–32.
8. F. Ghorbani, S. Kamari, S. Zamani, S. Akbari, M. Salehi, Optimization and modeling of aqueous Cr (VI) adsorption onto activated carbon prepared from sugar beet bagasse agricultural waste by application of response surface methodology, *Surface. Interfac*, 2020; 18: 100444.
9. V. thiQuyen, T.H. Pham, J. Kim, D.M. Thanh, P.Q. Thang, Q. Van Le, S.H. Jung, T. Kim, Biosorbent derived from coffee husk for efficient removal of toxic heavy metals from wastewater, *Chemosphere*, 2021; 284: 131312.
10. D.R. Saad, Z.T. Alismaeel, A.H. Abbar, Cobalt removal from simulated wastewaters using a novel flow-by fixed bed bio- electrochemical reactor, *Chem. Eng. Process - Process Intensif*, 2020; 156: 108097.
11. C. Peterson and T. K. Kwei, *J.Phys. Chem*, 1961; 65: 1330.
12. P.P.Vishwakarma, A. K. Singh and V. N. Singh., *Asian Environ*, 1989; 11(3): 49.
13. K. P. Yadav, B. S. Tyagi and V. N. Singh., *J. Environ. Tech. Letters*, 1988; 9(11): 1233.
14. K. Chaturvedi, K.C. Pathak and V. N. Singh., *J. Applied ClayScience.*, 1988; 3: 337.
15. J. K. Edzwaid., *Chem. Abs*, 1977; 86: 95708z.
16. Goswami and M. K. Purkait, “Removal of fluoride from drinking water using nanomagnetite aggregated schwertmannite,” *Journal of Water Process Engineering*, 2014; 1: 91–100.
17. L. Zheng, Z. Dang, X. Yi, H. Zhang, Equilibrium and kinetic studies of adsorption of Cd (II) from aqueous solution using modified corn stalk, *J. Hazard Mater*, 2010; 176 (1–3): 650–656.
18. K.H. Park, P.K. Parhi, N.H. Kang, Studies on removal of low content copper from the sea nodule aqueous solution using the cationic resin tp 207, *Separ. Sci. Technol*, 2012; 47(10): 1531–1541.