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Article

Removal of Cadmium(II) Using Red Powdered Marble Waste from Aqueous Matrix

P. K. Baroliya*, Ankita Shrimali, Varsha Dayma, Jaishri Chopra

Department of Chemistry, Mohanlal Sukhadia University, Udaipur, Rajasthan, India

ABSTRACT

This report describes use of Red Powdered Marble Waste (RPMW) for the removal of Cd^{2+} from aqueous matrix. RPMW is considered as inexpensive and widespread solid waste which is directly exposed to environment. The removal of Cd^{2+} ions from aqueous medium is achieved by optimizing various adsorption parameters along with the effect of temperature, pH, stirring time, and Cd^{2+} ion concentration. Kinetic studies were carried out using Morris-Weber equation. Langmuir and Freundlich adsorption isotherms are successfully employed for the study of adsorption of Cd^{2+} ions onto RPMW. Thermodynamic parameters specifically Gibbs free energy change (ΔG), enthalpy (ΔH), and entropy (ΔS) have also been calculated and their values −4.537 KJ/mol, 68.53 KJ/mole, and 16.8621 J/mole, respectively. The highest removal of Cd^{2+} ion onto RPMW was found to be 340.59 mg/gm. These findings suggested that the adsorption process of Cd(II) ion onto RPMW was endothermic and spontaneous in nature.

Key words: Red marble, Cadmium, Adsorption, Waste water.

1. INTRODUCTION

The rapid industrializations have elevated release of heavy metals to the environment, creating huge problems worldwide. Heavy metals are known to be toxic and their effect on human population and related health hazards have been widely studied [1]. Heavy metal contamination in water is released by numerous industries, particularly mining, metal plating, process, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries, and storage batteries industries [2]. Disposal of industrial waste and effluents to environment is a major source of heavy metals contamination to earth surface and ground water. The major disadvantages of heavy metal contaminations are non-biodegradable substance that accumulates in living organisms [3].

Cadmium is one of the toxic heavy metals, which has a large number of toxic effects to human health. Its intake to humans results in various health problems such as high blood pressure and destruction of kidneys and red blood cells [4,5]. The concentration of Cd^{2+} 0.005 mg/L is permitted as threshold value should not be exceeded for maintaining ecological equilibrium [6,7].

While toxic metal management is largely focused on prevention of water resources from contamination and heavy metals discharging at very low concentration, but heavy metals contamination can be minimized by removing metal contamination from industrial waste water. In the literature, a number of technologies have been reported for wastewater treatment, which include adsorption, ion exchange, electrochemical processes, precipitation, and membrane filtration technology. All these chemical-based methods are proved to be less efficient and expensive [8]. Among these methods, adsorption process is most commonly used and economically favorable method [9]. Various adsorbents such as powdered marble slurry [10], fuller earth [11], neem bark [12], and saw dust [13] have been used for the removal of toxic metals.

In the present investigation, Red Powdered Marble Waste (RPMW) adsorbent is used for the removal of Cd^{2+} ions from synthetic solutions. The composition of adsorbent was confirmed by Fourier transform infrared (FTIR) and qualitative analysis. Surface analysis was also done using atomic force microscopy (AFM). The effect of adsorption parameters such as pH of medium, temperature, metal ion concentration, and contact time on the removal of Cd^{2+} was also optimized. The developed method was effectively applied for the removal of cadmium from synthetic solutions.

2. METHODOLOGY

2.1. Apparatus

Quantification of Cd^{2+} ion was done by atomic adsorption spectrophotometer (Elico SL 168). For stirring, an auto stop magnetic stirrer (IKA) was used and pH of solutions was measured by Milwaukee pH meter. The FTIR spectra of RPMW were recorded on Bruker ALPHA-T spectrometer. AFM (model NT-MDT SOLVER NEXT, Moscow, Russia) from the Department of Physics Mohanlal Sukhadia University, Udaipur, was used for particle size determination in close contact mode.

2.2. Materials

Stock solutions of Cd^{2+} were prepared from $Cd(NO_2)_2$ by dissolving 0.247 g in 1000 mL demineralized water and dilution was made as and

***Corresponding author:**
E-mail: prabhatkbaroliya@mlsu.ac.in

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when required. RPMW adsorbent was collected from marble processing unit located in RIICO area of Chittorgarh (Rajasthan, India). The sieved RPMW of 63 µm size was used for the whole experiment. To remove soluble impurities present, RPMW first washed with demineralized water, the process repeated in triplicates and then dried for 24 h in oven. The functional group of RPMW was characterized through FTIR analysis. The observable peaks at about 710, 875, 1441, 1085, and 2516 agreed with $CaCO_3$ [14]. The RPMW sample contained 19.33% of SiO_2, 2.39% of Fe_2O_3, 3.39% of A Tsai l_2O_3, 36.08% of CaO, and 4.22% of MgO as analyzed from volumetric analysis. Particle size of the RPMW analyzed using AFM, as illustrated in Figure 1, identified microparticles of size bellow 0.344 µm.

2.3. Procedure

To optimize favorable condition for adsorption, various parameters were studied. Effects of Cd^{2+} ion concentration (100–1000 mg/L) followed by pH (2–10) and temperature (15–50°C) on adsorption were examined for 1 gm/L of RPMW solution. Stirring time has also been examined from 15 to 55 min on magnetic stirrer. After each study, quantification of unadsorbed Cd^{2+} ion was made using AAS. The adsorption percentage (A) and metal uptake (q_e) of Cd^{2+} ion onto RPMW have been calculated using Equations 1 and 2, respectively.

$$A = \frac{c_i - c_r}{c_i} \times 100 \quad (1)$$

$$q_e = \frac{c_i - c_r}{m} \times v \quad (2)$$

Where, c_i: initial concentration of Cd^{2+} ions, c_r: residual concentration of Cd^{2+} ions, v: volume of suspension, and m: weight of the adsorbent.

3. RESULTS AND DISCUSSION

This paper expands study on batch adsorption of Cd^{2+} onto RPMW. The adsorption of Cd^{2+} onto RPMW has been found to 100% under the optimum conditions, i.e. 1 g/L RPMW, pH=7.0, stirring time of 30 min, and 700 mg/L of Cd^{2+}concentration.

3.1. Influence of Metal Concentration, pH, and Temperature on Adsorption

Concentration of adsorbent is an important parameter in adsorption experiment. Percentage of adsorption of Cd^{2+} ions onto RPMW decreases with increasing its concentration, as shown in Figure 2. It was highest up to 700 mg/L of Cd^{2+} ions, decrease in the adsorption with increasing metal ion concentration can be explained in terms of relatively small number of active sites of adsorbent at higher concentration of Cd(II) ions in the solutions.

The pH of medium plays a key role in adsorption of metal ions from aqueous matrix since it affects the solubility of the metal ions. Effect of pH of the solution was studied, RPMW has excellent adsorption in the pH range of 5–8, as described in Figure 3. At pH below 2, the adsorption is very low because at low pH $CaCO_3$ and $MgCO_3$ get solubilize in solution and above pH 9, metal ion undergoes possible hydrolysis; thus, adsorption percentage decreases. Thus, pH 7 has been selected for further studies as an optimum condition.

3.2. Kinetics of the Adsorption

The effect of stirring time on adsorption of Cd^{2+} ion onto RPMW studied by varying stirring time and kinetics of adsorption was studied by Morris-Weber equation [15] (Eq. 3). The initial rapid adsorption onto RPMW indicated that the adsorption process arises mostly on the surface of RPMW.

$$q_t = k_d \sqrt{t} \quad (3)$$

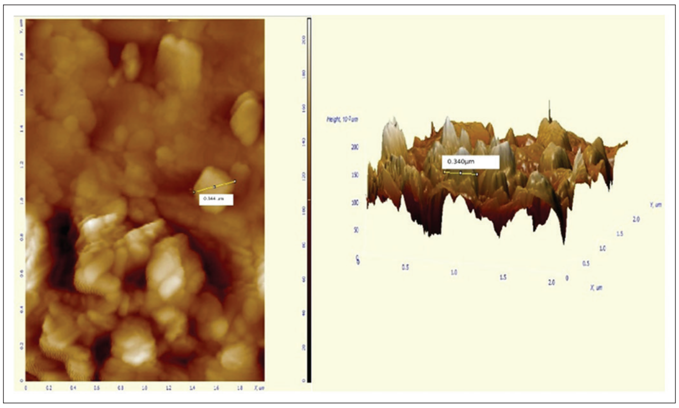

Figure 1: Atomic force microscopy image of red powdered marble waste.

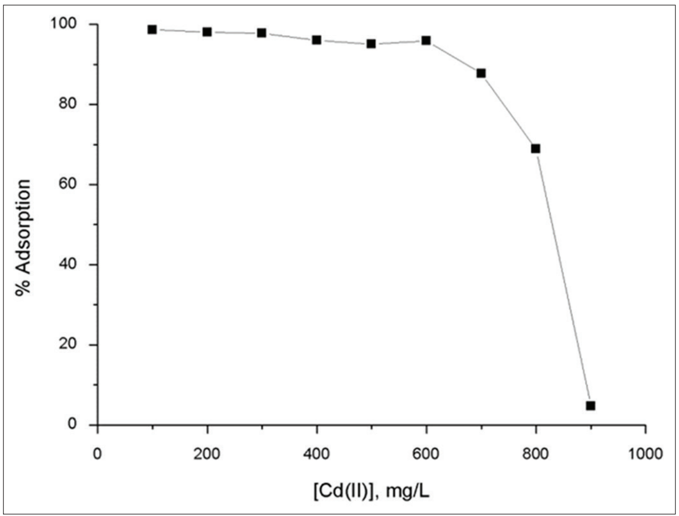

Figure 2: Effect of Cd^{2+} concentration on adsorption.

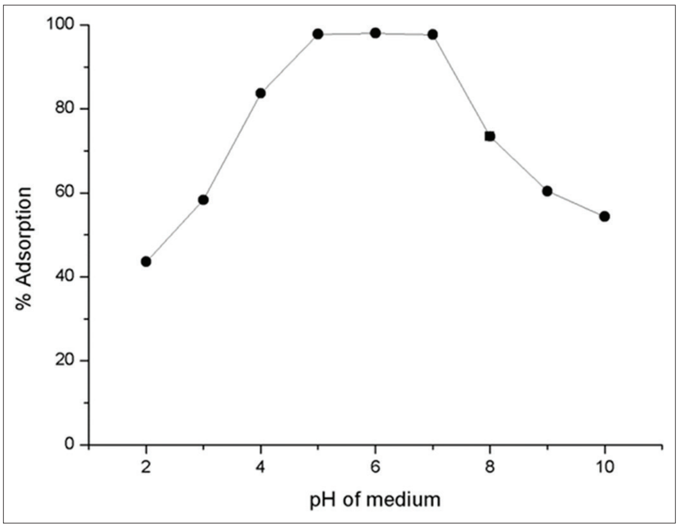

Figure 3: Effect of pH on adsorption.

Where, q_t: amount of Cd^{2+} ions adsorbed (mg/g) at time t and k_d: rate constant.

To calculate rate constant, q_t was plotted against $\sqrt{t}$, as described in Figure 4. Rate constant (k_d, 503.22 (mg/gm)/min) shows the mobility of Cd^{2+} ions toward marble slurry surface [16,17].

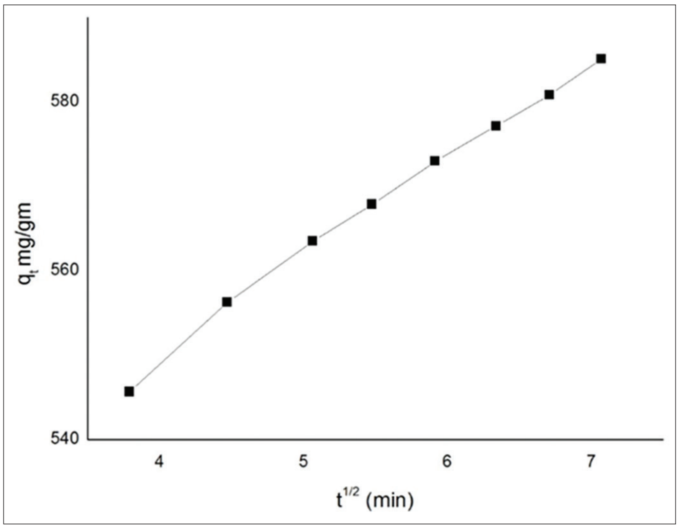

Figure 4: Plot of amount of Cd(II) adsorbed against square root of time.

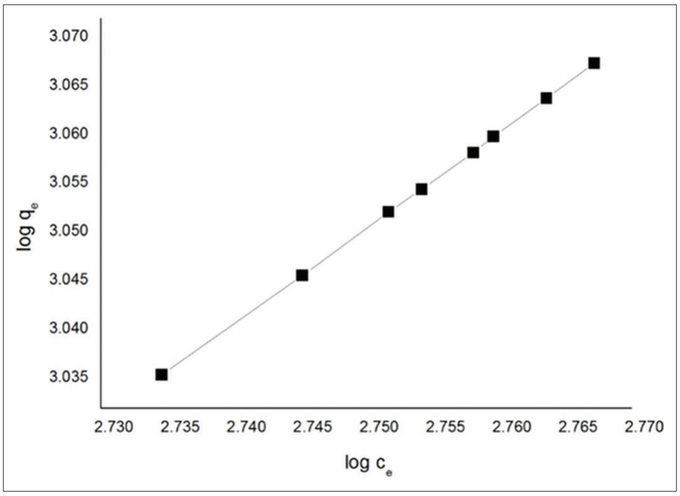

Figure 5: Freundlich plot for Cd(II) ions adsorption by red powdered marble waste.

3.3. Adsorption Isotherms

Freundlich and Langmuir adsorption isotherms used to provide various information related to adsorption processes. From results (Figures 5 and 6), it has been observed that both isotherms well described by system at room temperature.

Freundlich adsorption isotherm is written in linear form as

$$Log\ q_e = log\ k_f + 1/n\ log\ c_e \tag{4}$$

Where, q_e: amount of cadmium ion adsorbed (mg/g), K_f: indicator of adsorption capacity, 1/n: intensity of adsorption, and C_e: concentration of Cd^{2+} (mg/g) at equilibrium.

Parameters n and k_f were calculated through slope (1.00402 L/g) and intercept (2.05) by plotting a graph between q_e and c_e with correlation coefficient of 0.99998. The greater than unity value of n is suggested favorable adsorption of Cd^{2+} ion on RPMW [18,19].

Langmuir adsorption isotherm is written in linear form as follows, which is used to determine the adsorption capacity of RPMW.

$$C_e/q_e = c_e/q_m + 1/q_m b \tag{5}$$

Where, q_m: adsorption capacity (mg/g) and 1/b: free energy of adsorption.

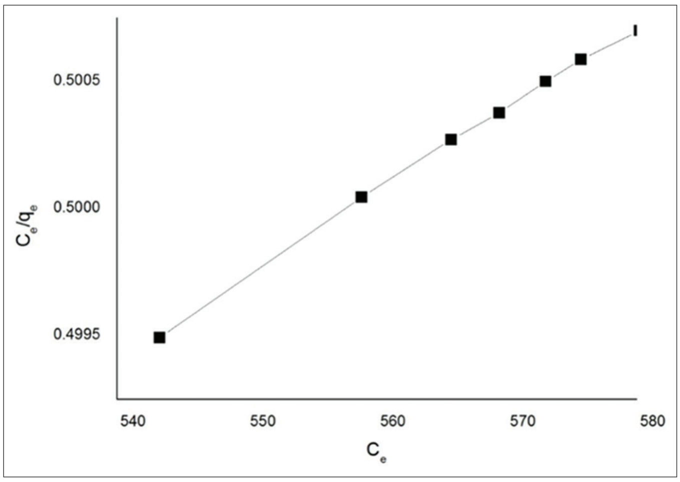

Figure 6: Langmuir plot for Cd(II) ions adsorption by Red Powdered Marble Waste.

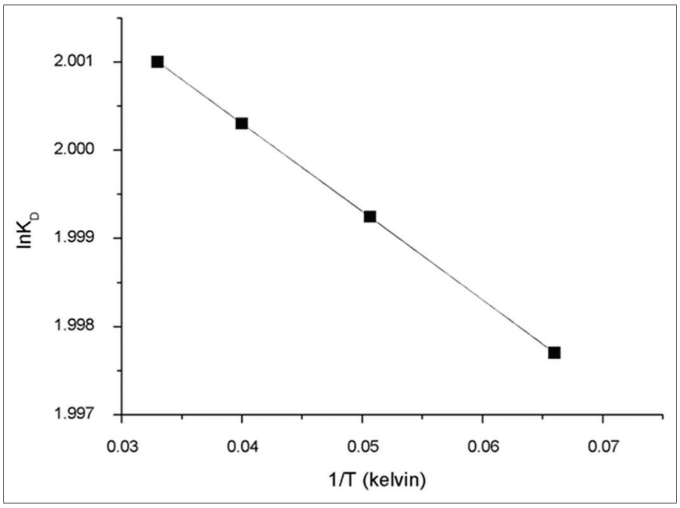

Figure 7: Thermodynamic distribution coefficient calculated for the adsorption of Cd(II) ions by red powdered marble waste.

When the equation was applied to the system, it gave a linear plot on plotting a graph between c_e/q_e and c_e. This model also suggested that the coverage of metal ion is of monolayer type on outer surface of RPMW [20]. The values of q_m (340.58786, mg/g) and b (1420.11, mL/g) were calculated using slope and intercept, respectively.

3.2.1. Thermodynamics of adsorption

Von't Hoff equation to calculate Gibbs free energy is given as,

$$\Delta G = -RT\ ln\ K_d \tag{6}$$

Where, k_d: equilibrium constant which is ratio q_e and c_e.

The following equation has been used to determine spontaneity of a process.

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

$$ln\ k_d = -\Delta H/RT + \Delta S/R \tag{8}$$

Where, T: temperature and R: universal gas constant having value 8.314 J/mol K.

On plotting a graph between lnk_d and 1/T, values of enthalpy, entropy, and Gibbs free energy have been calculated from slope, intercept, and Equation-7, respectively, which are as follows:

ΔH=68.532 KJ/mol, ΔS=16.862 J/mol K, ΔG=−4.53 KJ/mol.

Spontaneity and feasibility of this adsorption process are indicated by the negative value of ΔG, as calculated from graph (Figure 7). Positive value of ΔH and ΔS indicates that the adsorption process is endothermic and irreversible, respectively.

4. CONCLUSION

The experimental data of adsorption models for the removal of Cd^{2+} were well described by Langmuir and Freundlich adsorption isotherms. The results show that the mechanism of removal of Cd^{2+} ions onto RPMW is the physisorption and partially chemisorption at surface. It has been observed that on increasing temperature, the adsorption capacity increases describing that the adsorption process was partially chemical in nature. The spontaneity and endothermic nature of the process are also ascertained by thermodynamic parameters.

5. REFERENCES

1. M. Jaishankar, T. Tseten, N. Anbalagan, B. B. Mathew, K. N. Beeregowda, (2014) Toxicity, mechanism and health effects of some heavy metals, ***Interdisciplinary Toxicology***, **7:** 60-72.
2. A. Malik, (2004) Metal bioremediation through growing cells, ***Environmental International***, **30:** 261-278.
3. S. Rengaraj, Y. Kim, C. K. Joo, J. Yi, (2004) Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: Kinetics and equilibrium, ***Journal of Colloid and Interface Science***, **273:** 14-21.
4. S. E. Ghazy, G. A. E. Mostafa, (2008) Separation of cadmium(II), murcury(II), bismuth(III) and antimony(III) from drinking and river waters by flotation, ***Canadian Journal of Analytical Sciences and Spectroscopy***, **53:** 28-35.
5. S. E. Ghazy, (1995) Removal of cadmium, lead, mercury, tin, antimony and arsenic from drinking and seawaters by colloid precipitate flotation, ***Separation Science and Technology***, **30:** 933-947.
6. Z. W. Zhang, C. S. Moon, T. Watanabe, S. Shimbo, F. S. He, Y. Q. Wu, S. F. Zhou, D. M. Su, J. B. Qu, M. Ikeda, (1997) Background exposure of urban populations to lead and cadmium, comparison between China and Japan, ***International Archives of Occupational and Environmental Health***, **69:** 273-281.
7. H. Babich, G. Stotzky, (1985) Heavy metal toxicity to microbe mediated ecologic processes, a review on potential application to regulatory policies, ***Environmental Research***, **36:** 111-137.
8. P. Preetha, T. Viruthagiri, (2005) Biosorption of zinc(II) by Rhizopusarrhizus; Equilibrium and kinetic modeling, ***African Journal Biotechnology***, **4:** 506-508.
9. E. S. Bailey, T. J. Olin, R. M. Bricka, D. D. Adrian, (1999) A review of potentially low-cost sorbents for heavy metals, ***Water Research***, **33:** 2469-2479.
10. M. Bhalothia, N. Suman, P. K. Baroliya, R. Dashora A. K. Goswami, (2016) Marble slurry waste as a scavenger material for Cr(III) ions from aqueous medium, ***Desalination and Water Treatment***, **57:** 17377-17383.
11. J. U. K. Oubagaranadin, N. Sathyamurthy, Z. V. P. Murthy, (2007) Evaluation of Fuller's earth for the adsorption of mercury from aqueous solutions: A comparative study with activated carbon, ***Journal of Hazardous Material***, **142:** 165-174.
12. Islamuddin, R. K. Gautam, N. F. Siddique, N. More, (2016) *Azadirachta indica* (Neem) leaf powder used as a natural adsorbent for the removal of chromium Cr (VI) from an aqueous solutions, ***International Research Journal of Engineering and Technology***, **3:** 2234-2239.
13. Mishra, V. Tadepalli, S, (2015) Biosorption of toxic heavy metals on sawdust. ***Clean Soil Air Water***, **43:** 360-367.
14. W. T. Tsai, J. M. Yang, C. W. Lai, Y. H. Cheng, C. C. Lin, C. W. Yeh, (2006) Characterization and adsorption properties of eggshell and eggshell membrane, ***Bioresource Technology***, **97:** 488-493.
15. W. J. Weber, S. C. Morris, (1963) Intraparticle diffusion during the sorption of surfactants onto activated carbon, ***Journal of the Sanitary Engineering Division by American Society of Civil Engineers***, **89:** 53-61.
16. S. A. Asheh, F. Banat (2001) Adsorption of zinc and copper ions by the solid waste of the olive oil industry. ***Adsorption Science Technology***, **19:** 117-129.
17. S. E. Ghazy, A. H. M. Gad, (2010) Lead separation by sorption onto powdered marble waste. ***Arabian Journal of Chemistry***, **7:** 277-286.
18. S. Akhtar, R. Qadeer, (1997) Active carbon as an adsorbent for lead ions. ***Adsorption Science Technology***, **15:** 815-824.
19. E. Erdem, N. Karapinar, R. Donat, (2004) The removal of heavy metal cations by natural zeolites. ***Journal Colloid Interface Science***, **280:** 309-314.
20. C. Aharoni, M. Ungarish (1977) Kinetics of activated chemisorption Part 2 theoretical models. ***Journal of Chemical Society Faraday Transactions***, **73:** 456-464.