Journal of Advances and Scholarly Researches in Allied Education
Vol. 20, Issue No. 2, April-2023, ISSN 2230-7540

A Study on Low-Cost Adsorption Kinetics for the removal of Heavy Metal Ions from Water Sample

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Abstract - Toxic, non-biodegradable heavy metal contaminants found in industrial effluents have been shown to accumulate in humans and other animals via the food chain. Natural geological weathering, processing of ores, usage of metals, landfill trash, livestock, animal and human excrements, urban run-off, and re-use of drainage water and sewage effluents all contribute to the issue, which is most common in places with high concentrations of industry. Heavy metals also infiltrate water via agricultural usage of metal coating, insecticides, fertilizers, etc. Industrial effluents include heavy metal ions like cadmium(II) and chromium(VI), which are hazardous and non-biodegradable and may accumulate in humans via the food chain. Pseudo-first and second order models were used. Different kinetic models have been developed to analyze experimental data in order to learn more about the factors that influence the rate of adsorption of cadmium (II) and chromium (VI) ions onto various adsorbents.

Keywords - Low Cost, Adsorption, Kinetic, Heavy Metal Ion, Water

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INTRODUCTION

Large quantities of heavy metals may be discharged into the environment as a result of improper industrial waste disposal methods. Zinc, chromium, copper, cobalt, cadmium, nickel, lead, iron, and arsenic are all typical heavy metals. Although humans need trace quantities of a few of these metals, even these low levels of exposure pose health risks, and much larger levels of exposure may be hazardous. Non-biodegradability of heavy metals makes them much more hazardous owing to the poisonous heavy metals' bioaccumulation impact in living creatures, which might have negative outcomes. Batteries, metallurgy, mining, paint, transportation, building, and dyeing are all major contributors to air pollution caused by heavy metals. As an added bonus, zinc is employed in the production of antimicrobial cotton textiles in addition to its more common uses in alloying and galvanizing. Zinc is utilized in microdoses for the medical treatment of organisms, but it may be toxic in larger doses. The EPA has established a $5mgl^{-1}$ maximum contaminant level for zinc in potable water. Therefore, it is of the utmost importance that the zinc be successfully extracted from the water. The finest adsorbent for efficiently extracting zinc is activated carbon, but its expensive price has prevented its widespread use in industry. Both organic and inorganic contaminants contribute to environmental degradation. Heavy metal ions, which are highly poisonous and carcinogenic, pose the greatest threat to the modern world. Heavy metal contamination is linked to human actions and their effects on the ecosystem's food web. Industries such as petrochemical, textile, tannery, plastic, mining, battery, paint and pigment, paper and pulp, and many more all contribute to the environmental pollution caused by heavy metals. The release of harmful metals into water streams is a major cause for worry since it might compromise the safety of our drinking water. Arsenic, mercury, chromium, cadmium, and lead are all examples of heavy metal ions that may be harmful to human health.

LITERATURE REVIEW

Maharana, & Manna, Madhumita & Sardar, Moumita & Sen, Sujit (2021) One of the most pressing environmental problems today is polluted water. Since heavy metals remain in the environment, cleaning them up is a pressing issue. Heavy metal contamination in water and soil systems is caused by activities such as mining, electroplating, and the production of fertilizer. Arsenic, lead, and cadmium are just a few of the metals that may be found in drinking water, and they pose serious health risks. Toxic metal poisoning of lakes, rivers, and other water bodies has worsened as industrial activity has increased. Therefore, it is important to find a way to purge heavy metals from effluent water that is both kind to the environment, economical, and effective.

Panda, Laxmipriya & Jena, Sandeep & Rath, Swagat & Misra, Pramila (2020) In this research, a geopolymer was synthesized from dolochar ash and employed for the adsorption-based removal of Co(II), Ni(II), Cd(II), and Pb(II) from an aqueous solution. The geopolymer was studied using several analytical methods. Dolochar ash's crystallinity was destroyed during geoploymerization, as shown by the XRD pattern. The presence of a peak at 982 cm1 in the FTIR spectrum, attributable to Si-O-Si and Si-O-Al bonds, provided conclusive evidence of geopolymer production. The material was shown to be mesoporous based on BET surface area tests. Adsorption trials showed that the geopolymer was more effective in removing the pollutants than the feed dolochar ash. In order to maximize metal ion removal efficiency, the impacts of several experimental parameters were analyzed. These factors included pH, temperature, reaction duration, and starting metal ion concentration. The pseudo-second-order rate equation was used to describe the adsorption process, proving that Langmuir's model was correct.

Ugwu, et al (2020) This article provides a summary of the adsorption techniques for removing heavy metals using inexpensive adsorbent. The drawbacks of several of the methods employed to sequester metal ions throughout the years include, among other things, the production of sludge and high operating expense. The adsorption technique employing inexpensive adsorbents has been shown to be both financially viable and ecologically benign. In this overview, we look at the research done on many different inexpensive adsorbents for the removal of heavy metals. According to the studies we looked at, increasing the contact duration, temperature, starting concentration, adsorbent dose, and lowering the pH resulted in greater chromium, copper, and zinc removal percentages.

Hussain, Athar & Madan, Sangeeta & Madan, Richa. (2021) Heavy metal removal using adsorption methods is widely employed in wastewater treatment. Although activated carbon produces excellent results and is hence the most popular adsorbent, its high price makes it impractical for widespread application. It's expensive to make and hard to replenish. There is an urgent need to find substitutes that put less strain on the world's dwindling supply of freshwater. In addition, heavy metals are harmful even at low concentrations, therefore inexpensive adsorbents were needed for a green solution to their cleanup. Adsorption has become popular because of the benefits it provides at low cost in terms of waste management. This chapter is unique because it compares and contrasts the efficacy of a broad variety of adsorbents in removing heavy metals from wastewater.

Chakraborty, et al (2020) Heavy metal ion contamination in wastewater is a major source of environmental degradation and one of the world's most pressing problems. Ion exchange, chemical precipitation, coagulation, membrane separation, reverse osmosis, and adsorption are only some of the typical procedures that have been employed to remove heavy metal ions under the name of remediation. There are several adsorbents available for use in the removal of heavy metal ions from wastewater, especially those that have been shown to be toxic to living creatures. When compared to more traditional approaches, adsorption technologies are more cost-effective and may effectively remove heavy metal ions at trace concentrations. Here, we take a look at how effective different natural waste materials and their modified forms are in filtering out metals from drinking water and wastewater. The primary goal has been to amass complete information on the removal of heavy metal ions using inexpensive adsorbents.

RESEARCH METHODOLOGY

Kinetics

Different kinetic models have been used to look at actual data in order to figure out how adsorption works and what steps might affect the rate, such as mass transfer, film diffusion, pore diffusion, and chemical reaction processes. The rates of cadmium ion adsorption onto ANI (APC and PPC), LGB (APC and PPC), and CAC were studied by doing tests with 50 mL cadmium solutions with different starting amounts ranging from 10 mg/dm^3 to 40 mg/dm^3. 0.1N HCl and 0.1N NaOH were used to bring the pH to 5.5, and the solution was mixed with adsorbent of size 75-90µ and a dose of 5g/dm^3 for different amounts of time, up to 300 minutes, at a temperature of 303±1K.

Pseudo-first order model: Lagergren came up with the pseudo-first order model for how solutes get taken out of a liquid in 1898. The equation for the pseudo-first-order rate is

$$\frac{dq}{dt} = k_1 (q_e - q_t) \quad (1)$$

By applying the boundary constraints t = 0 to t = t and q = 0 to q = q, we may integrate equation (1) to get the following integral form:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (2)$$

In this equation, k_1 is the first order adsorption rate constant (min^{-1}) and qt and q_e are the milligrams of metal ions adsorbed per gram of adsorbent at a particular time and equilibrium, respectively.

Pseudo-second order model: Assuming that the adsorption capacity is proportional to the number of active sites occupied on the adsorbent, we may rewrite the kinetic rate law to get a pseudo-second order rate equation to characterize the adsorption kinetics, as shown below.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

By integrating across the intervals t = 0 to t = t and qt = 0 to qt = qt, the resulting boundary conditions are given by Equation (3).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Here, k_2 is the second-order adsorption rate constant, and qt and q_e are the milligrams of solute adsorbed per gram of adsorbent at time t and equilibrium, respectively. Assigning an efficient q_e is not a difficulty in Equation (4).

Adsorption Isotherm

Adsorption systems are best designed with the help of the equilibrium adsorption isotherm. Adsorption capacity is determined by equilibrium investigations of the adsorbent. Adsorption isotherms characterize this phenomenon, and their constants provide information about the adsorbent's surface characteristics and affinity.

- **Effect of adsorbent dose:**

Using batch studies at a temperature of 303±1K and a metal ion solution concentration of 50 mg/dm^3, we determined that the removal efficiency of Cd(II) ions by ANI (APC & PPC), LGB(APC & PPC), and CAC increased as the adsorbent dosage increased. Using 0.1N NaOH and 0.1N HCl, the pH of the solution was adjusted to 5.5, and then the solutions were equilibrated with 0.4g to 8g/dm^3 of each adsorbent, with particle sizes ranging from 75 to 90 microns, for six hours at 225 rpm in a mechanical rotary shaker. After an equilibrium period, the solutions were withdrawn from the shaker, filtered with whatmann number 40 filter paper, and analyzed to determine the concentration of residual metal ions; the results are shown in Fig. 1.

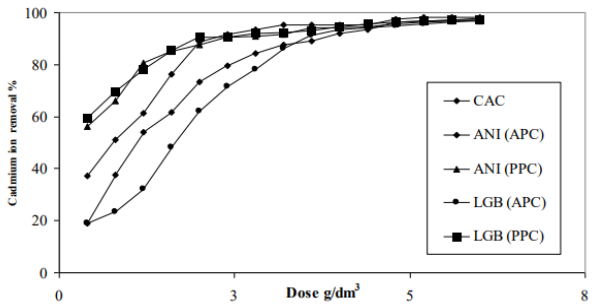

Figure 1: Effect of adsorbent dose on cadmium ion removal for different adsorbents (CO: 50mg/dm^3; pH: 5.5; T: 303±1K; Size: 75- 90µ; Time: 6hours)

- **Effect of particle size:**

The impact of adsorbent particle size on the removal of cadmium ion by various adsorbents was studied in a batch adsorption study employing 12 distinct particle sizes ranging from below 75 microns to 850 microns. Fig. 2 depicts the correlation between adsorbent particle size and metal removal efficiency. With further reduction in particle size, the proportion of cadmium ions removed has risen. Smaller particles have a greater surface area, which leads to a greater rate of clearance.

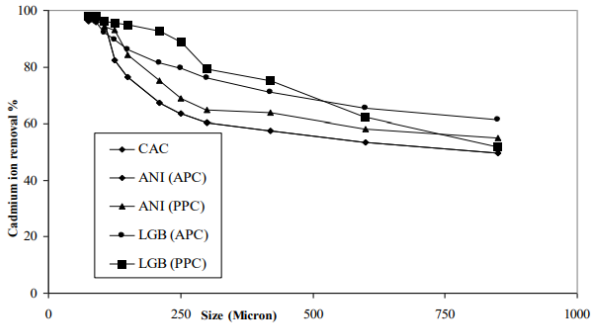

Figure 2: Effect of adsorbent size on the removal of cadmium ion for different adsorbents (pH: 5.5; T: 303±1K; CO: 50mg/dm^3; Dose: 5g/dm^3; Time: 6 hours)

Desorption and Recovery of Adsorbents

One of the most important considerations for evaluating the economic viability of adsorbents is their desorption. In order to renew the adsorbents and reuse the water, we first analyzed the adsorption of cadmium ions onto ANI (APC & PPC), LGB (APC & PPC), and CAC. Below, we discuss our findings about the desorption of adsorbed cadmium ions from APC, PPC, and CAC. Metal ion adsorbed adsorbents that were maintained on the filter paper after adsorption studies were performed using 50 mL of 40mg/dm^3 of cadmium ion of each adsorbent at pH 5.5 were collected and washed thoroughly with double-distilled water to eliminate any unadsorbed Cd(II) ion.

DATA ANALYSIS

Kinetics

Pseudo-first and pseudo-second order rate equations (equations 2 and 4) were used to fit the influence of contact duration on chromium(VI) ion removal. The initial adsorption rate (h) was calculated using equation 5 (Table 1), and for pseudo-second order, this was done by analyzing plots of t/qt against t for different initial concentrations of chromium(VI) ions. Pseudo-first order equations were found to have r2 values much lower than 0.99, indicating that they are unable to adequately characterize the kinetics. An expression for the initial adsorption rate, h, at t→0 is

$$h = k_2 q_e^2 \quad (5)$$

Pseudo-second-order kinetics provides a fair approximation for the adsorption process, as shown by the excellent fits seen for the plot of t/qt versus t across all concentrations.

Table 1: Pseudo-first order/second order kinetic parameters obtained by linear methods at different initial chromium(VI) ion concentrations for different adsorbents (pH 2.0; T: 303±1 K; Dose: 4g/dm^3; Size: 75-90 μ)

Pseudo-first order parameters				Pseudo-second order parameters				Adsorbents
Conc. C_o (mg/dm^3)	q_e (mg/g)	k_1 X 10^{-2} (min^{-1})	r^2	q_e (mg/g)	k_2 (g/mg min) X 10^{-2}	h (mg/g min)	r^2	
10	0.82	1.45	0.9899	2.41	16.91	1.57	1.0000	ANI (APC)
20	0.44	1.06	0.9397	4.79	9.48	2.17	1.0000	
30	0.30	1.70	0.9737	7.13	5.19	2.45	1.0000	
40	0.15	1.60	0.9734	9.51	2.71	2.64	1.0000	
10	0.23	1.93	0.9565	2.47	7.69	0.47	0.9999	LGB (APC)
20	0.11	1.70	0.9644	4.88	2.76	0.66	0.9999	
30	0.50	1.98	0.9688	7.31	1.32	0.71	0.9998	
40	0.66	1.89	0.9773	9.73	0.81	0.76	0.9997	
10	1.05	1.29	0.9523	2.43	26.51	1.52	1.0000	ANI (PPC)
20	0.40	1.36	0.9860	4.83	8.53	1.97	1.0000	
30	0.31	1.36	0.9417	7.03	5.69	2.87	1.0000	
40	0.60	1.69	0.9431	9.28	3.80	3.36	1.0000	
10	0.82	1.27	0.9798	2.44	44.62	2.62	1.0000	LGB (PPC)
20	0.33	1.24	0.9477	4.80	9.88	2.30	1.0000	
30	0.20	1.11	0.9738	7.10	7.64	3.77	1.0000	
40	0.04	1.02	0.9508	9.40	4.56	3.93	1.0000	
10	0.73	0.90	0.9675	2.45	17.52	1.05	0.9999	CAC
20	0.26	1.13	0.9694	4.83	6.62	1.54	0.9998	
30	0.15	0.88	0.9652	7.09	4.47	2.24	0.9998	
40	0.03	0.87	0.9576	9.39	2.90	2.56	0.9997	

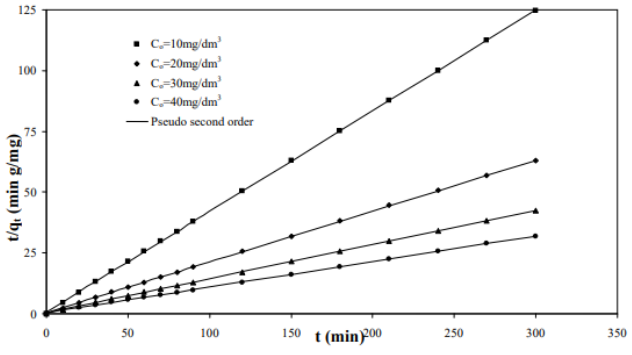

Figure 4: Type 1 Pseudo-second order linear equation obtained by using linear method for the adsorption of chromium(VI) ions onto ANI (APC) at various initial concentrations (pH: 2.0; T: 303±1K; Dose: 4g/dm^3; Size: 75-90 μ)

Adsorption Isotherm

All five adsorbents were tested in tests using a 50 mL solution of Cr(VI) ion at starting concentrations ranging from 10 to 100 mg/dm^3. The solution was adjusted to a pH of 2.0. All adsorbents were applied at the same rate of 4g/dm^3. For 6.5 hours, the solution was agitated at 225 rpm in a rotary shaker set to a temperature of 303±1K.

- **Effect of adsorbent dose:**

Using batch studies at a temperature of 303±1K and a metal ion solution concentration of 40mg/dm^3, we determined that the removal efficiency of Cr(VI) ion by ANI (APC & PPC), LGB(APC & PPC), and CAC varied as a function of adsorbent dosage. After bringing the solution to a pH of 2 with 0.1N NaOH and 0.1N HCl, the solutions were equilibrated with 0.4g to 8g/dm^3 of each adsorbent, with particle sizes ranging from 75 to 90 microns, in a mechanical rotary shaker operating at 225rpm for 6.5 hours.

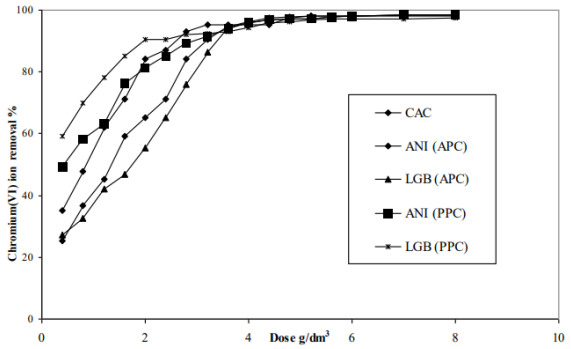

Figure 5: Effect of adsorbent dose on chromium(VI) ion removal for different adsorbents (C0: 40mg/dm^3; pH: 2.0; T:303±1K; Size: 75-90μ; Time: 6.5 hours)

- **Effect of particle size**

The influence of adsorbent particle size on the removal of chromium(VI) ion by various adsorbents was investigated in batch adsorption tests employing 12 distinct particle sizes ranging from 75 micron to 850 micron. The tests were performed using a metal ion solution of 40mg/dm^3 in a volume of 50mL. A mechanical rotary shaker operating at 225rpm was used to equilibrate the solution with 4g/dm^3 of adsorbent of varied sizes for 6.5 hours after the pH was lowered to 2 using 0.1N NaOH and 0.1N HCl.

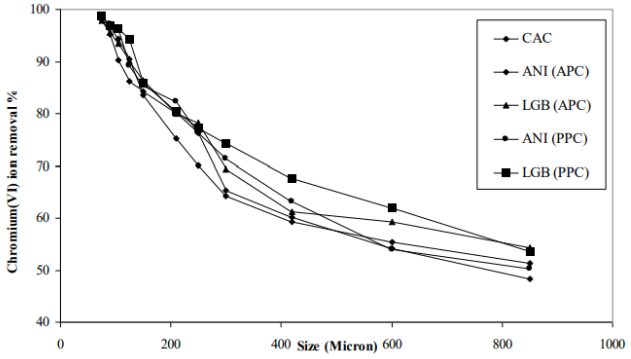

Figure 6: Effect of adsorbent sizes on the removal of chromium(VI) ion for different adsorbents (pH: 2; T:303±1K; C0:40mg/dm^3; Dose: 4g/dm^3; Time: 6.5 hours)

Desorbtion and Recovery of Adsorbents

Steps were made to recover the metal ions that would aid in the regeneration of the adsorbents and the recycling of the water after the study of the adsorption of chromium(VI) ion onto ANI (APC& PPC), LGB (APC& PPC), and CAC. The nature of the adsorption process may also be better understood with the use of desorbtion research. Here, we look at how APC, PPC, and CAC deal with the loss of adsorption of chromium(VI) ions. The metal ion adsorbed adsorbents that were kept on the filter paper after adsorption tests were performed using 50 mL of 20mg/dm^3 of chromium ion solution with individual adsorbents at pH 2. This was followed by a thorough washing with DD water to remove any unadsorbed Cr(VI) ion. Then, for 2 hours, 100 mL of NaOH (from 0.01 to 0.1M) was mixed with the metal-loaded adsorbents.

CONCLUSION

Adsorption kinetics research validates the Yushan Ho and McKay's pseudo-second order kinetic model. The intraparticle diffusion model has also been fitted to the kinetic findings. For several adsorbents, graphs of qt vs $t^{1/2}$ were not linear and did not intersect at zero. The optimal size of adsorbents was determined to be between 75 and 90 microns by studying the impact of particle size variation on the % removal of cadmium and chromium ions. The research also showed that adsorbents made from the wood of these two trees treated by acid and pyrolysis may be utilized to effectively remove cadmium and chromium ions at a reasonable cost. Research on the effect of adsorbent size on the removal of chromium(VI) ion shows that more removal occurs with smaller adsorbent sizes. For each experiment, 75-90µ was shown to be the optimal adsorbent size.

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