



Temperature impact on pollutant removal from wastewater and water using adsorption techniques

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Abstract

Recent research (Workers 37–40) has increasingly focused on the contamination of surface waterways and groundwater by heavy metals, driven by environmental and industrial factors. Given that a significant portion of the population relies on surface and groundwater for drinking purposes, the escalation of global water pollution due to heavy metals like Mercury, Copper, Zinc, Lead, Nickel, Cobalt, Iron, Manganese, Cadmium, and Chromium has been pronounced over the past decades. These metals have long been a major concern in water pollution, heightened by public awareness following incidents of heavy metal poisoning in aquatic environments. Notable events include the Itai-Itai disease outbreak in Japan associated with cadmium-contaminated river water, the transformation of inorganic mercury into methyl mercury with its bioaccumulation effects, the carcinogenic properties of certain inorganics and metals, and the potential use of recycled wastewater to supplement drinking water supplies in the near future, all contributing to renewed scrutiny on heavy metal contamination.

Heavy metals are byproducts generated in numerous industrial activities, encompassing chemical manufacturing, fertilizer production, leather processing, metal finishing (including polishing and cleaning), metallurgy, electroplating, refractory operations, textile mills, wood processing, and various others. The concentrations and types of metals present in industrial wastewater can vary widely, ranging from suspended metal particles to metal ions and complexes dissolved in solution. Companies involved in the processing of non-metallic materials also generate effluents containing metals.

Keywords: Temperature, removal, pollutants, wastewater, adsorption technique

1. Introduction

Through the mass transfer process known as adsorption, components from the liquid phase are moved into the solid phase, where they accumulate as a surface layer of solute molecules on the adsorbent. Adsorbent is the solid, liquid, or gas phase on which the adsorbates accumulate. Adsorbate is the material that is being extracted from the liquid phase at the interface. Surface forces or surface energy that are out of equilibrium lead to adsorption, which encompasses both physical and chemical causes. Chemical adsorption methods entail the formation of ion complexes and the establishment of chemical bonds between the adsorbate and adsorbent, whereas physical adsorption mechanisms result from molecule condensation in the capillaries of the solid. The specifics of the atomic species involved determine the bonding's exact nature. Adsorption can be broken down into three distinct processes: ^[1] bulk solution transport, which moves the adsorbate across the fixed film boundary layer

surrounding the adsorbent media by means of advection and dispersion ^[2], diffusive transport, which moves the adsorbate across the fixed film boundary layer, and ^[3] binding processes, which act to bind the adsorbate to the media surface. The rate of solute molecule diffusion within the pores of the adsorbent particles regulates the overall rate of adsorption. The rate rises as a function of temperature, solute molecular weight, and adsorbate concentration.

It is very important to investigate how temperature affects how quickly and thoroughly pollutants are removed from wastewater and water using the adsorption process. The rate of absorption of adsorbate species generally decreases with temperature increase 1–13. Because of the weakening of the adsorptive pressures between the active sites of the biosorbent and adsorbate species, the process is known as exothermic. However, there are also instances where the temperature of the system causes an increase in the uptake of molecules or ions. Endothermic adsorption is this kind of

adsorption [14-29]. The breakage of some internal bonds along the border of the active surface sites of the biosorbent, according, increases the number of adsorption sites, which in turn increases the amount of adsorption. Because the rate process controls the amount of time that the adsorbate and biosorbent are in touch with each other, understanding the pace at which the removal of pollutants reaches a state of thermodynamic equilibrium is highly helpful. Therefore, in order to apply this technique and achieve the best possible removal of a specific adsorbate by an appropriate biosorbent, it is required to investigate the effect of temperature on the rate of adsorption and residence time for various systems under research.

This study examines how *Mucor heimalis* and *Spirogyra* sp. remove Cd (II), Pb (II), and Cr (VI) in response to temperature. We calculated the rate constants for the uptake of Cd (II), Pb (II), and Cr (VI). Studies on intraparticle diffusion have been done. Studies on mass transfer from the biosorbent's bulk to its surface have also been done.

2. Materials and Methods

The selection of metal ions and biosorbents plays a pivotal role in the effectiveness of biosorption for removing contaminants. Both the rate and capacity of removal are significantly influenced by these factors. Biosorbents vary widely in their chemical composition depending on their source, necessitating thorough characterization to elucidate the mechanisms underlying the sorption of Cd(II), Pb(II), and Cr(VI). The effectiveness of sorption is contingent upon the specific sorbate species and the elemental composition of the sorbents. This chapter explores the origins, concentrations, and toxicity of adsorbates in aqueous systems, incorporating findings from various physico-chemical techniques used to analyze and characterize these adsorbents.

2.1 Procedure

In the current experiments, adsorption progress was monitored using a batch mode of operation. This involved shaking 1.0 gram of selected adsorbents, *Mucor heimalis* and *Spirogyra* sp., with 50 mL of aqueous solutions containing cadmium chloride, lead nitrate, and potassium dichromate. The shaking was conducted at a constant speed of 125 rpm in various glass bottles. Prior to each

experiment, the pH of the adsorbate solutions was adjusted using appropriate strengths of HCl and NaOH. The adsorption process was tracked at regular intervals until saturation was achieved. Residual adsorbate concentrations were determined by analyzing the supernatant liquid using an atomic absorption spectrophotometer and an ion selective titrator plus system (Orion Ion Selective Titrator plus System, model no. 960, manufactured by Thermo Orion, USA) after specific time intervals.

To account for potential adsorption on the internal surfaces of the bottles, blank experiments were conducted under identical conditions of concentration, pH, and temperature but without adding any adsorbent.

At 20, 30, and 40°C, the adsorbates of Cd (II), Pb (II), and Cr (VI) were studied for their ability to bind to a variety of biosorbents, with starting concentrations of 125, 400, and 150 mg L⁻¹, respectively.

3. Results and Discussion

The effect of temperature on the removal of Cd (II), Pb (II), and Cr (VI) by various biosorbents indicates that the uptake of these adsorbate species at each temperature is sufficiently rapid in the initial stages of adsorption and then it gradually decreases with the passage of time until the attainment of saturation. After this, adsorption remains constant.

Also highlighted is the smoothness, continuity, and approach to saturation of these curves. According to the data collected at various temperatures, the saturation time is not temperature-dependent. However, a change in temperature has a significant impact on the rate and amount of sorption.

As the temperature of the system increases from 20 to 40°C at a pH of 8.1 and an initial concentration of 125 mg L⁻¹, the percentage uptake of Cd (II) via adsorption on *Mucor heimalis* and *Spirogyra* sp. declines from 97.20 to 86.35 and 94.5 to 81.54, respectively (Table.1). With a rise in temperature from 20 to 40°C at a pH of 6.5 and an initial concentration of 400 mg L⁻¹, the percentage adsorption for the removal of Pb (II) by *Mucor heimalis* and *Spirogyra* sp. likewise falls (Table 2). The percentage of Cr (VI) removed by *Mucor heimalis* and *Spirogyra* sp. at pH 2.0 increases from 86.13 to 97.45 and 80.30 to 93.45, respectively, with initial concentrations of 150 mg L⁻¹ as temperature increases from 20 to 40°C (Table 3), in contrast to these observations.

Table 1: Effect of temperature on the removal of cd(ii) by different biosorbent

Concentration:		125 mg L ⁻¹	Agitation speed:		125 rpm
pH:		8.1	Particle size:		<180 μm
Biosorbent	Adsorbate	Temperature (°C)	Amount adsorbed (mgg ⁻¹)	% Removal	Equilibrium Time (min.)
<i>Mucor heimalis</i>	Cd (II)	20	6.07	97.20	100
		30	5.76	92.15	
		40	5.39	86.35	
<i>Spirogyra</i> sp.	Cd (II)	20	5.91	94.50	110
		30	5.52	88.33	
		40	5.10	81.54	

Table 2: Effect of temperature on the removal of pb (ii) by various biosorbents

Concentration:		400 mg L ⁻¹	Agitation speed		125 rpm
pH:		6.5	Particle size:		<180 μm
Biosorbent	Adsorbate	Temperature (°C)	Amount adsorbed (mgg ⁻¹)	% Removal	Equilibrium Time (min.)
Mucor heimalis	Pb (II)	20	19.10	95.50	100
		30	17.90	89.65	
		40	16.60	83.00	
Spirogyra sp.	Pb (II)	20	18.00	90.00	120
		30	16.90	84.35	
		40	15.50	77.55	

Table 3: Effect of temperature on the removal of cr (vi) by various biosorbents

Concentration:		150 mg L ⁻¹	Agitation speed:		125 rpm
pH:		2.0	Particle size:		<180 μm
Biosorbent	Adsorbate	Temperature (°C)	Amount adsorbed (mgg ⁻¹)	% Removal	Equilibrium Time (min.)
Mucor heimalis	Cr (VI)	20	6.46	86.13	130
		30	6.91	92.08	
		40	7.30	97.45	
Spirogyra sp.	Cr (VI)	20	6.02	80.30	140
		30	6.52	86.87	
		40	7.01	93.45	

The change in chemical potential, which is connected to the solubility of the adsorbates, can be used to explain the variation in adsorption extent with temperature. If the adsorbate species' solubility grows with temperature, the chemical potential lowers, and both of these effects-the adsorbate species' solubility and the impacts of normal temperature-work in the same direction. As a result, adsorption will decrease. Adsorption may decrease or increase depending on the dominant factor in other circumstances where the temperature has the opposite impact on the solubility of the adsorbate. The adsorption of Pb(II), Cd(II), and Cr(VI) by Mucor heimalis and Spirogyra sp. decreased with system temperature rise in the current investigation, but Cr(VI) adsorption by the same biosorbent increased with system temperature increase. The fact that Cr (VI) ions require a specific amount of energy to pass the potential barrier across the solid-solution interface, equivalent to the term energy of activation, Ea, which may be derived, may also be used to explain the rising propensity of adsorption with temperature.

By charting the values of log Kad Vs 1/T, which results in a straight line, one can calculate the values of activation energy, Ea, at various temperatures. This confirms that adsorption tends to increase with temperature. Given that each biosorbent is porous and that it is possible for adsorbate species to diffuse, the process that controls how much adsorption increases with temperature may be endothermic diffusion. As a result of their research, Knocke and Hemphill33 have also offered a similar justification. The decrease in Cd (II) and Pb (II) adsorption with increasing temperature is a sign that the forces that bind the adsorptive sites of the biosorbent and adsorbate species together are diminishing. Lal and colleagues34 have proposed this explanation.

3.1 Effect of temperature on adsorption kinetics

The Lagergreen rate equation was used to graphically compute the adsorption rate constant kad of Cd (II), Pb (II),

and Cr (VI) removal by chosen biosorbents at various temperatures. The results clearly show that the values of kad at various temperatures correspond to the degree of adsorption with regard to temperature.

For several biosorbent-adsorbate systems, the rate constant of intraparticle diffusion (kid) was derived from the slopes of the corresponding linear plots of q vs. For each adsorbate-biosorbent system under study, the values of kid thus obtained support the trend of adsorption with regard to temperature.

3.2 Thermodynamic parameters

For the adsorption of Cd (II), Pb (II), and Cr (VI) on various biosorbents, changes in standard free energy (G0), enthalpy (H0), and entropy (S0) have been used to explain the variation in the adsorption with regard to temperature. The subsequent formulae were used to calculate these:

Table 4: Adsorption rate constant kad and rate of intraparticle diffusion kid for different adsorbate- biosorbent system

Biosorbent	Adsorbate	Temperature (°C)	kad (min ⁻¹)	kid mgg ⁻¹ min-1/2
Mucor heimalis	Cd (II)	20	6.080	1.19 X 10 ⁻²
		30	5.711	1.20 X 10 ⁻²
		40	5.366	8.36 X 10 ⁻³
Spirogyra sp.	Cd (II)	20	5.896	1.08 X 10 ⁻²
		30	5.343	9.83 X 10 ⁻³
		40	4.836	8.05 X 10 ⁻³

Table 5: Adsorption rate constant kad and rate of intraparticle diffusion kid for different adsorbate- biosorbent system

Biosorbent	Adsorbate	Temperature (°C)	kad (min ⁻¹)	kid mgg ⁻¹ min-1/2
Mucor heimalis	Pb (II)	20	4.675	6.88 X 10 ⁻³
		30	4.261	6.23 X 10 ⁻³
		40	3.915	5.45 X 10 ⁻³
Spirogyra sp.	Pb (II)	20	4.600	6.25 X 10 ⁻³
		30	4.168	5.68 X 10 ⁻³
		40	3.800	5.05 X 10 ⁻³

Table 6: Adsorption rate constant k_{ad} , rate of intraparticle diffusion k_{id} and activation energy e_a for different adsorbate-biosorbent system

Biosorbent	Adsorbate	Temperature ($^{\circ}$ C)	$k_{ad} \text{ min}^{-1}$	$k_{id} \text{ mgg}^{-1} \text{ min}^{-1/2}$	$E_a \text{ kcal mol}^{-1}$
		20	4.422	8.21×10^{-3}	
Mucor heimalis	Cr (VI)	30	4.675	9.13×10^{-3}	1.778
		40	5.389	10.5×10^{-3}	
		20	3.938	7.89×10^{-3}	
Spirogyra sp.	Cr (VI)	30	4.215	8.77×10^{-3}	1.237
		40	4.514	9.65×10^{-3}	

Tables include the values of the thermodynamic parameters that were so determined. These statistics make it clear that all of the systems' tiny and negative free energy change values indicate that the process is spontaneous. Such circumstances allow the adsorptive forces to overcome the potential barrier. The removal of Cd (II) and Pb (II) by adsorption is thought to be exothermic, according to the negative values of standard enthalpy change (H^0) in Tables, whereas the removal of Cr (VI) by various biosorbents at various temperatures is thought to be endothermic. The values of H^0 for the majority of cases imply higher binding between the ions adsorbed and the active surface sites of the biosorbents, as is seen from Tables. It is impossible to rule out the potential of simultaneous occurrence of physical and chemical adsorption to varying degrees in such circumstances. At this point, it is challenging to make any definite predictions concerning the type of adsorption. In the

case of Cd (II) and Pb (II) removal by adsorption on various biosorbents at different temperatures, the negative values of entropy change (S^0) imply a faster interaction during the forward process (adsorption). It is anticipated that the association, fixation, or immobilisation of Cd(II) and Pb(II) during the adsorption process will reduce the degree of freedom of the adsorbate ions, leading to a decrease in entropy. However, the rise in translational entropy brought on by the randomization of displaced water molecules from the surface of biosorbents may be the cause of the positive entropy change (S^0) in the case of Cr (VI).

The results of the studies mentioned above demonstrate that one of the most crucial factors in the prevention of water contamination is temperature. Environmentalists will find this to be very useful when building the water treatment facility where these metals are pollutants.

Table 7: Thermodynamic parameters for adsorption of Cd (Ii) on to different biosorbents at various temperatures

Biosorbent	Adsorbate	Temperature ($^{\circ}$ C)	$\Delta G^0 \text{ kcal mol}^{-1}$	$\Delta H^0 \text{ kcal mol}^{-1}$	$\Delta S^0 \text{ call mol}^{-1} \text{ K}^{-1}$
		20	-2.048	-18.589	-56.454
Mucor heimalis	Cd (II)	30	-1.484	-11.853	-34.22
		40	-1.141		
		20	-1.662		
Spirogyra	Cd (II)	30	-1.218	-14.684	-44.444
sp.		40	-0.926	-10.055	-29.165

Table 8: Thermodynamic parameters for adsorption of pb (ii) on to different biosorbents at various temperatures

Biosorbent	Adsorbate	Temperature ($^{\circ}$ C)	$\Delta G^0 \text{ kcal mol}^{-1}$	$\Delta H^0 \text{ kcal mol}^{-1}$	$\Delta S^0 \text{ call mol}^{-1} \text{ K}^{-1}$
		20	-1.7786		
				-16.093	-48.855
Mucor heimalis	Pb (II)	30	-1.2902		
				-15.237	-46.029
		40	-0.9860		
		20	-1.2792		
				-8.845	-25.822
Spirogyra	Pb (II)	30	-1.0211		
sp.				-8.659	-25.208
		40	-0.7690		

Table 9: Thermodynamic parameters for adsorption of cr(vi) on to different biosorbents at various temperatures

Biosorbent	Adsorbate	Temperature ($^{\circ}$ C)	$\Delta G^0 \text{ kcal mol}^{-1}$	$\Delta H^0 \text{ kcal mol}^{-1}$	$\Delta S^0 \text{ call mol}^{-1} \text{ K}^{-1}$
		20	-1.0633		
				11.186	41.806
Mucor heimalis	Cr (VI)	30	-1.4811		
				21.418	75.575
		40	-2.2372		
		20	-0.8170		
				8.679	32.410
Spirogyra	Cr (VI)	30	-1.1410		
sp.				14.425	51.373
		40	-1.6548		

4. Conclusion

According to research on how temperature affects the adsorption of Cd(II), Pb(II), and Cr(VI), a rise in temperature decreases the extent and pace of Cd(II) and Pb(II) adsorption, whereas a rise in temperature promotes the removal of Cr(VI). The equilibrium period, however, is unaffected by temperature. At various temperatures, the rate constant of sorption has been calculated using first order kinetics. The rate constant of intraparticle transport has been computed at various temperatures, which suggests that Cd(II), Pb(II), and Cr(VI) uptake rates employing different biosorbents are controlled by diffusion. The rate-limiting phase has been verified by determining the pore diffusion coefficient. Numerous thermodynamic parameters have also been calculated, and sources are also provided.

In a solid-liquid system, the concentration of solutes on the solid surface and their uptake from the solution increase until reaching equilibrium. This dynamic continues until the concentration of solutes on the surface and in the solution stabilize. The equilibrium is influenced by factors such as the nature of the adsorbent, temperature, type of solute, pH, particle size, among others, and is particularly sensitive to the initial solute concentration. Understanding adsorption equilibrium is crucial for designing heterogeneous chemical processes and constructing reactors used in adsorption-based waste treatment. Adsorption isotherms provide valuable insights into the extent of surface coverage by the adsorbent, offering fundamental information essential for optimizing adsorption processes.

5. References

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