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A study of the effect of temperature on removal of pollutants from wastewater and water by adsorption technique

Anamika Singh and Dr. Ashok Kumar

Abstract
Workers37-40 have recently become interested in studies on the heavy metal contamination of surface waterways and ground waters. This was caused by both environmental and industrial factors, as well as the fact that the majority of people got their drinking water from surface and ground water. Water pollution from many heavy metals, such as Mercury, Copper, Zinc, Lead, Nickel, Cobalt, Iron, Manganese, Cadmium, and Chromium, has significantly and globally increased over the past few decades. These heavy metals have long been a key source of worry regarding water pollution. The public's awareness of toxicity has grown following a number of incidents involving accidents brought on by heavy metal poisoning in aquatic environments. The Itai-Itai disease outbreak in Japan linked to the use of cadmium-rich river water, the discovery of inorganic mercury's conversion to methyl mercury and its bio-accumulation, the carcinogenicity of some inorganics and metals, and the potential for recycling wastewater to supplement drinking water in the near future are some of the other factors that have brought heavy metals back into the spotlight.
Heavy metals are produced as waste in a variety of industrial processes, including the production of chemicals, fertilisers, leather, metal finishing (metal polishing and metal cleaning), metallurgical processes, electroplating, refractory units, textile and wood mills, and others. Metal concentrations in different industrial wastewaters can vary greatly in terms of quality and quantity. From pure metal particles in suspension to metal ions and complexes in solution, metals can be found in wastewater in a variety of forms. Metal-containing effluents are produced by a number of companies that process non-metallic materials.

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 [14-20]. The breakage of some internal bonds along the border of the active surface sites of the biosorbent, according to Navrot *et al*., 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. Research Methodology

The type of metal ion and the biosorbents used in the process have a significant impact on the removal of contaminants using the biosorption approach. Both the rate and the capacity of the removal are significantly impacted. Depending on the source, the chemical makeup of sorbents varies greatly from sample to sample. Characterizing them is crucial to ensure a better understanding of the mechanism of Cd (II), Pb(II), and Cr(VI) sorption since the nature of sorption depends on the sorbate species and the elements of the sorbents. The origins, concentrations, and toxicity of adsorbates in the aqueous system are discussed in this chapter, which also incorporates the outcomes of several physico-chemical techniques used to characterize the adsorbents.

2.1 Procedure

To track the advancement of adsorption in the current experiments, the batch mode of operation was chosen. The process involved shaking 1.0 gm of desired grade adsorbent, namely Mucor heimalis and *Spirogyra* sp., with 50 mL of an aqueous solution of the adsorbate, namely cadmium chloride, lead nitrate, and potassium dichromate, at a constant speed of 125 rpm in various glass bottles. Prior to each run of the experiment, the pH of the adsorbate solution was adjusted by adding HCl and NaOH of the appropriate strength. Up until saturation was reached, the adsorption process was tracked at various intervals. The residual adsorbate concentration was 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, made by Thermo Orion, USA), after the completion of predetermined time intervals.

To account for any adsorption on the inside surface of the bottles, blanks were always run without adsorbent under identical concentration, pH, and temperature conditions.

At 20, 30, and 400C, 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. Result 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 400C 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 400C 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 400C (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 (^{0}C)**	**Amount adsorbed (mgg^{-1})**	**% Removal**	**Equilibrium Time (min.)**
Mucor heimalis	Cd (II)	20	6.07	97.20	
		30	5.76	92.15	100
		40	5.39	86.35	
Spirogyra sp.	Cd (II)	20	5.91	94.50	
		30	5.52	88.33	110
		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 (^{0}C)**	**Amount adsorbed (mgg^{-1})**	**% Removal**	**Equilibrium Time (min.)**
		20	19.10	95.50	

Mucor heimalis	Pb (II)	30	17.90	89.65	100
		40	16.60	83.00	
		20	18.00	90.00	
Spirogyra sp.	Pb (II)	30	16.90	84.35	120
		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 (^{0}C)**	**Amount adsorbed (mgg^{-1})**	**% Removal**	**Equilibrium Time (min.)**
		20	6.46	86.13	
Mucor heimalis	Cr (VI)	30	6.91	92.08	130
		40	7.30	97.45	
		20	6.02	80.30	
Spirogyra sp.	Cr (VI)	30	6.52	86.87	140
		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 k_{ad} and rate of intraparticle diffusion k_{id} for different adsorbate- biosorbent system

Biosorbent	**Adsorbate**	**Temperature (^{0}C)**	**k_{ad} (min^{-1})**	**k_{id} mgg-1 min-1/2**
		20	6.080	1.19 X 10^{-2}
Mucor heimalis	Cd (II)	30	5.711	1.20 X 10^{-2}
		40	5.366	8.36 X 10^{-3}
		20	5.896	1.08 X 10^{-2}
Spirogyra sp.	Cd (II)	30	5.343	9.83 X 10^{-3}
		40	4.836	8.05 X 10^{-3}

Table 5: Adsorption rate constant k_{ad} and rate of intraparticle diffusion k_{id} for different adsorbate- biosorbent system

Biosorbent	**Adsorbate**	**Temperature (^{0}C)**	**k_{ad} (min^{-1})**	**k_{id} mgg-1 min-1/2**
		20	4.675	6.88 X 10^{-3}
Mucor heimalis	Pb (II)	30	4.261	6.23 X 10^{-3}
		40	3.915	5.45 X 10^{-3}
		20	4.600	6.25 X 10^{-3}
Spirogyra sp.	Pb (II)	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 (^{0}C)	k_{ad} min^{-1}	k_{id} mgg-1 min-1/2	E_a kcal mol^{-1}
		20	4.422	8.21 X 10^{-3}	
Mucor heimalis	Cr (VI)	30	4.675	9.13 X 10^{-3}	1.778
		40	5.389	10.5 X 10^{-3}	
		20	3.938	7.89 X 10^{-3}	
Spirogyra sp.	Cr (VI)	30	4.215	8.77 X 10^{-3}	1.237
		40	4.514	9.65 X 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 (H0) in Tables, whereas the removal of Cr (VI) by various biosorbents at various temperatures is thought to be endothermic. The values of H0 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 (So) 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 (So) 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 (^{0}C)	ΔG^0 kcal mol^{-1}	ΔH^0 kcal mol^{-1}	ΔS^0 cal mol^{-1} 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		
				-14.684	-44.444
Spirogyra	Cd (II)	30	-1.218		
sp.				-10.055	-29.165
		40	-0.926		

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

Biosorbent	Adsorbate	Temperature (^{0}C)	ΔG^0 kcal mol^{-1}	ΔH^0 kcal mol^{-1}	ΔS^0 cal mol^{-1}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 (^{0}C)	ΔG^0 kcal mol^{-1}	ΔH^0 kcal mol^{-1}	ΔS^0 cal mol^{-1}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 adsorption from solution grew until equilibrium was established. This process keeps going until the surface solute concentration and the solute concentration that is still in the solution are in dynamic equilibrium. The nature of the adsorbent, the temperature, the kind of solute, the pH, the size of the particles, etc., all affect the equilibrium. Generally, it has been discovered that the equilibrium changes with initial solute concentration. For chemical processes, the design of heterogeneous chemical processes, and the construction of heterogeneous chemical reactors for the adsorption-based treatment of wastes, the study of adsorption equilibrium is essential. All adsorption isotherms share the same quality information regarding how much of the surface is covered by the adsorbent.

4.1 Conflict of Interest

Not available

4.2 Financial Support

Not available

5. References

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