

**THERMODYNAMIC STUDY FOR THE REMOVAL OF CR(VI) IONS ON MIXED BIOMASS  
SMBTB AND *PANNONIBACTER PHRAGMETITUS***

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**ABSTRACT**

Numerous physical, chemical, and biological mechanisms may cause the release of heavy metals into aquatic systems. The impacts of heavy metals on the environment and the effects of the environment on heavy metals are the two broad categories into which the aftereffects of these discharges can be divided. The diversity, density, species makeup of the population, and community structure of the first category may change depending on the environmental conditions. The quantity of heavy metal species in the effluent/water and residues heavily influences the type and intensity of alteration. Consequently, the physical-chemical processes occurring in effluents and aquatic systems have a notable, albeit indirect, influence on the biological reactions. The second classification emphasizes that changes in the speciation and harmfulness of heavy metals may be caused by circumstances in receiving waters. Such circumstances include a substantial anthropogenic and geochemical material contribution, the type of industrial effluents, suspended particles, and chelator content. (1) Longitudinal variations in colloidal particles, suspended solids, and natural/synthetic ligands, and (2) Vertical variations in redox conditions, level of blending, and densities of living life forms are used to define the aquatic environment. The aforementioned considerations have a significant impact on how metals behave in particular waterways. Examples of environmental effects on metals include methylation and a loss in metallic form. Similar to how suspended particles and associated sedimentation cause metals to sink to the bottom of natural water bodies, these processes also cause metals to accumulate there. Organic ligands and complex metal chlorides slow down the sorption process and prolong the occupation period in the effluent/water. Fundamentally, natural forces govern how metals diffuse, and variations in emission are reactions to those forces.

**KEY WORDS:** Heavy Metals, Removal, Environment, Pollution.

## **INTRODUCTION**

### **HEAVY METALS**

Various heavy metal contaminants were released and accumulated in the environment as a result of the recent rapid industrialization. Over a certain threshold, these heavy metal contaminants have deleterious effects. Given that they are poisonous, carcinogenic, and mutagenic by nature, they have a significant impact on plants, animals, and people. Because they are essential components of enzyme complexes, blood pigments, biological oxygen and electron transport systems, cofactors, bone formation, and reproduction, heavy metals are required in trace levels in biological systems. Additionally, they are used in the medical industry as dietary vitamins and mineral supplements, some of which have therapeutic effects and boost immunological function. Some heavy metals are essential for the evolution of oxygen in plants and are also employed as preservatives and fungicides.

According to a 2012 assessment from the Blacksmith Institute, 125 million people worldwide are at risk from industrial pollution. We can see from this research how serious this issue is, thus it calls for advanced technologies and a lot of work to change dangerous heavy metals into less toxic ones. Due to their reactivity, ionic bond, and oxidation state under a different situation, these metals present a number of challenges for cleanup. Although there are strict restrictions and allowable limits in place to prevent the discharge of certain heavy metal concentrations from municipal and industrial waste into drinking water. Metals in the water are primarily caused by wastewater produced during mining, smelting, metal plating, battery production, etc.

Several well-known heavy metals and metalloids are to blame for the poisoning of soil and water resources, including cadmium, mercury, chromium, lead, arsenic, copper, selenium, nickel, zinc, silver, cobalt, and uranium. Of them, Cd is one of the most well-known harmful environmental pollutants, whose widespread use for industrial reasons has sparked a number of problems with the environment and human health around the world. The European Water Framework Directive added Cd to its list of hazardous substances based on its toxicity (EC, 2000). 3 g/l is the recommended level of Cd in drinking water (WHO, 2011). The USEPA and China have set a 5-g/l Cd upper limit. Researchers have previously looked at the bioavailability, behavior, occurrence, and remediation of Cd in soil and groundwater.

## **HEAVY METAL POLLUTION**

Water resource pollution with potentially harmful heavy metals, such as arsenic, copper, lead, chromium, nickel, and mercury, is a serious issue on a global scale. Insufficient or excessive amounts of heavy metals (HMs) and other trace elements can have a variety of negative impacts on living things. Heavy metals are persistent, non-biodegradable, and very hazardous by nature. Their constant deposition near receiving water bodies may pollute the food chain. Additionally, if consumed for drinking or other purposes, it may bioaccumulate in fatty living tissue and constitute a threat to lives. Therefore, it is crucial to cleanse wastewater that has been contaminated with metal before releasing it into the environment, particularly into aquatic systems.

## **DEFINITION**

A typical collective term for groups of metals and metalloids with an atomic number between 63.5 and 200.6 and a density greater than 5.0 gm cm<sup>-3</sup> is "heavy metal".

## **SOURCES OF HEAVY METALS**

The pollution of water bodies by HMs results from both natural and anthropogenic sources, but in urban areas, activities like mining, smelting, municipal effluent discharge without sufficient treatment, sewage disposal, etc. are complicating the situation. The primary source of HM contamination in the aquatic system is discharge from industries like tanneries, electroplating, fertilizers, pesticides, batteries, ore refineries, alloy industries, pigment, fuel, photographic material manufacturers, explosive manufacturers, smelting of metalliferous, surface finishing aerospace, gasoline, radiator manufacturers, etc.

## **RESEARCH METHODOLOGY**

## **SAMPLE COLLECTION**

In order to lessen the impact of microbial activity on the physicochemical characteristics of

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wastewaters and to avoid the maximum standard errors, wastewater samples were collected from the outlets of the two chosen industries in plastic gallons of 10 litres during the winters of January.

### **ISOLATION OF Cr(VI) RESISTANT BACTERIA AND BIOCHEMICAL IDENTIFICATION**

By employing the spread plate technique and nutrient medium, serial dilution was used to isolate the bacterial strain from the collected effluent. The chromium-containing agar medium was used to develop the microbial colonies. For the purpose of identifying highly resistant microbial strains, agar plates were coated with a solution of Cr(VI) ions at concentrations ranging from 100 to 1500 mg/L. For three to five days, cultured plate incubation was observed. After the microorganisms had grown, successful colonies were examined for additional sub-culturing in order to produce the pure culture. In Yaazh Xenomics, Coimbatore, pure culture was biochemically identified. GN cards were used for the automated biochemical identification process.

### **THERMODYNAMIC STUDIES**

Adsorbate at equilibrium, type of adsorbents, and spontaneity of adsorption are all quantified by thermodynamic investigations. Also investigated is the temperature range for optimum adsorption. The key thermodynamic parameters were computed using the Van't Hoff and Clasius Clapeyron equations: change in Gibbs energy ( $G_0$ ), adsorption enthalpy ( $H_0$ ), and entropy ( $S_0$ ).

### **EFFECT OF SOLUTION PH**

By altering the pH in the range of 2.0 to 8.0, the effect of solution pH on the evacuation of Cr(VI) ions onto mixed biosorbent material was investigated. To the 100 mL of Cr(VI) ion solution, the ideal amount of mixed biomass (SMBTB and *Pseudomonas stutzeri*) was added. After the specified time interval, the flasks were removed, and the AAS method was used to determine the concentration of Cr(VI) ions in the filtrates (supernatant).

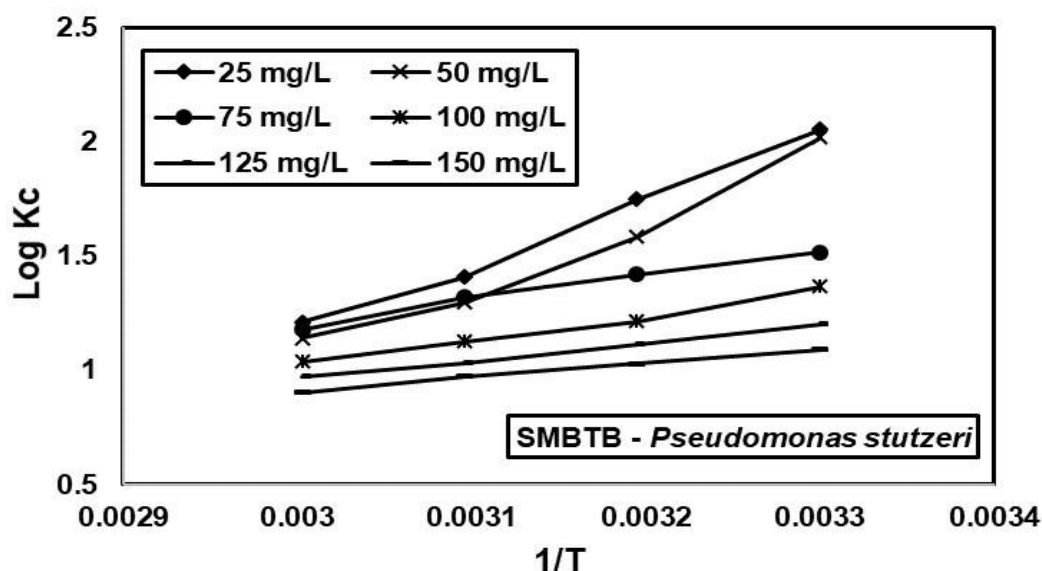
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## RESULTS AND DISCUSSION

### THERMODYNAMIC STUDY

Thermodynamic characteristics can be utilized to identify the exothermic or endothermic, spontaneity, and randomness of the Cr(VI) ion adsorption onto mixed biomass. Figures 4.39 and 4.40 depict the thermodynamic analysis for the removal of Cr(VI) ions from mixed biomass (SMBTB and *Pseudomonas stutzeri*, SMBTB and *Pannonibacter phragmetitus*).

The values of the thermodynamic parameters are shown in Tables, and a graph was drawn between  $\ln K_c$  and  $1/T$ . The tabulation report reveals that Gibbs free energy ( $G_0$ ) has negative values, indicating that the adsorption of Cr(VI) ions onto mixed biomass was naturally occurring and possible.



**FIGURE -1** Thermodynamic study for the removal of Cr(VI) ions onto mixed biomass (SMBTB and *Pseudomonas stutzeri*)

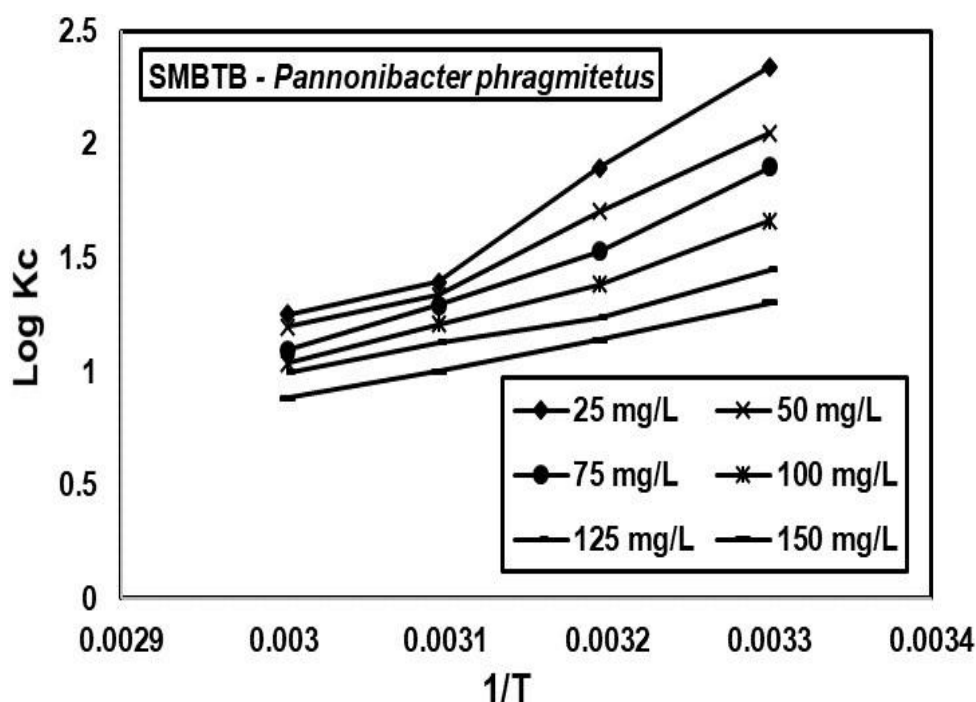


FIGURE-2 THERMODYNAMIC STUDY FOR THE REMOVAL OF CR(VI) IONS ONTO MIXED BIOMASS (SMBTB AND *PANNONIBACTER PHRAGMETITUS*)

TABLE-1 Adsorption thermodynamic studies for the removal of Cr(VI) ions onto mixed biomass (SMBTB and *Pseudomonas stutzeri*)

Conc. of Cr(VI) (mg/L)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol/K)	$\Delta G^\circ$ (KJ/mol)			
			30°C	40°C	50°C	60°C
25	-124.609	-320.16	-11.946	-10.410	-8.708	-7.738
50	-126.789	-331.63	-11.728	-9.402	-8.003	-7.289
75	-110.102	-286.16	-10.556	-8.930	-7.450	-6.710
100	-85.994	-214.36	-9.153	-8.000	-7.001	-6.106
125	-62.650	-146.45	-8.015	-6.820	-6.505	-5.759
150	-51.694	-117.29	-7.063	-6.330	-5.742	-5.321

**TABLE-2 ADSORPTION THERMODYNAMIC STUDIES FOR THE REMOVAL OF CR(VI) IONS ONTO MIXED BIOMASS (SMBTB AND PANNONIBACTER PHRAGMETITUS)**

Conc. of Cr(VI) (mg/L)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol/K)	$\Delta G^\circ$ (KJ/mol)			
			30°C	40°C	50°C	60°C
25	-165.152	-443.78	-13.525	-11.368	-8.625	-7.986
50	-127.036	-330.10	-11.863	-10.207	-8.263	-7.619
75	-114.365	-295.02	-11.003	-9.148	-7.942	-6.928
100	-87.885	-217.12	-9.604	-8.278	-7.496	-6.510
125	-61.612	-139.85	-8.417	-7.418	-6.912	-6.360
150	-57.436	-131.65	-7.509	-6.813	-6.102	-5.642

The adsorption process is described as being enthalpy-driven by the negative value of entropy change ( $S_o$ ), and the negative value of enthalpy change ( $H_o$ ) shows that the adsorption of Cr(VI) ions onto mixed biomass was exothermic in nature.

**EFFECT OF PH**

Figure illustrates the effect of pH on the evacuation of Cr(VI) ions from mixed biomass (SMBTB and *Pseudomonas stutzeri*, SMBTB and *Pannonibacter phragmetitus*).

When the pH was raised from 2.0 to 8.0, it was discovered from figure 4.41 that the removal percentage of Cr(VI) ions decreased. The electrostatic interaction between the mixed biomass and Cr(VI) ions occurred under potentially strongly acidic conditions. The functional groups will be protonated due to the abundant availability of H<sup>+</sup> particles at these low pH extends or high acidic pH extends. The active sites on the surface of mixed biomass have more particles carrying net negative charges when the pH is more than 2.0, which will generally repel the Cr(VI) ions.

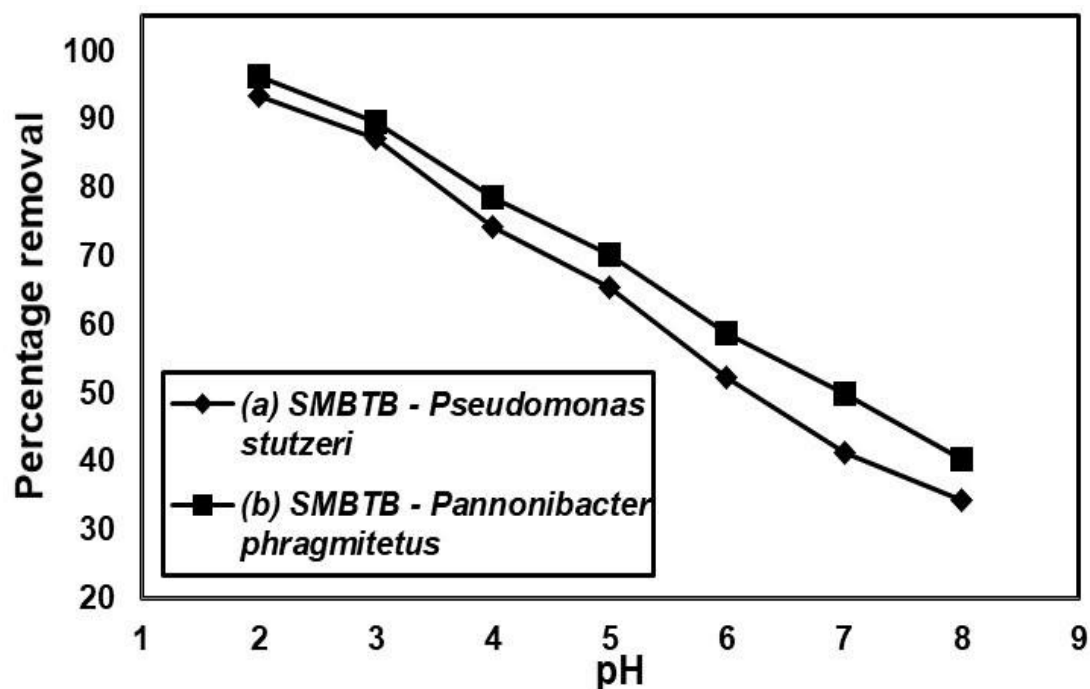


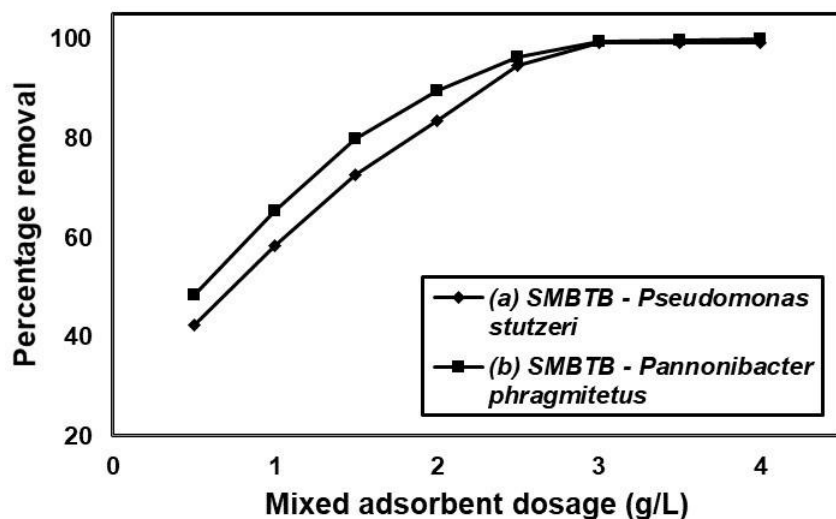
Figure-3 Effect of pH for the removal of Cr(VI) ions onto mixedbiomass

(Initial Cr(VI) ion concentration = 25 mg/L, SMBTB and *Pseudomonas stutzeri* = 3 g/L, time = 45 min and temperature = 30 °C) and (Initial Cr(VI) ion concentration = 25 mg/L, SMBTB and *Pannonibacter phragmitetus* = 3 g/L, time = 45 min and temperature = 30 °C)

#### EFFECT OF MIXED BIOMASS DOSAGE

Figure depicts the effects of the dose of mixed biomass on the evacuation of Cr(VI) ions onto mixed biomass (SMBTB and *Pseudomonas stutzeri*, SMBTB and *Pannonibacter phragmitetus*). When the dose of mixed biomass was increased from 0.5 g/L to 3.0 g/L, it was seen that the clearance percentage of Cr(VI) ions rose. The cause of this behavior was that as the dosage was increased, more surface active sites became accessible and were occupied by the Cr(VI) ions.





**Figure 4 Effect of mixed biomass dosage for the removal of Cr(VI) ions onto mixed biomass (SMBTB and *Pseudomonas stutzeri*; SMBTB and *Pannonibacter phragmetitus*)**

(Initial Cr(VI) ion concentration = 25 mg/L, time = 45 min, Ph = 2.0 and temperature = 30 °C)

#### COMPARISON OF MONOLAYER ADSORPTION CAPACITY

The findings of the comparison between the mixed biomass (SMTB and *Pseudomonas stutzeri*; SMTB and *Pannonibacter phragmetitus*) and other adsorbent materials for the removal of Cr(VI) ions are shown in Table 4.8. Mixed biomass (*Pseudomonas stutzeri*; SMTB and *Pannonibacter phragmetitus*) has a higher monolayer adsorption capacity, according to the tabulation report.

**TABLE - 3 COMPARISON OF MONOLAYER ADSORPTION CAPACITY OF MIXED BIOMASS FOR CR(VI) IONS ONTO DIFFERENT ADSORBENT MATERIALS**

S. No	Adsorbent	q <sub>m</sub> (mg/g)	References
1	Pineapple peel derived biochars	41.67	Shakya & Agarwal (2019)
2	SMBTB and <i>Pannonibacter phragmetitus</i>	31.5	This study
3	SMBTB and <i>Pseudomonas stutzeri</i>	27.47	This study
4	Clarified sludge	26.31	Bhattacharya et al (2008)
5	Magnetic biochar prepared from <i>Melia azedarach</i> wood	25.27	Zhang et al (2018)
6	Tannin-immobilized activated clay	24.09	Li et al (2012)
7	Paper mill sludge	23.18	Gorzin & Abadi (2018)
8	Red mud	21.1	Gupta et al (2001)
9	Bamboo bark based AC	18.94	Zhang et al (2015)
10	KOH activated Peanut shell	13.48	Al-Othman et al (2012)
11	Rice Husk	13.1	Sugashini & Begum (2015)
12	Activated charcoal	12.87	Mor et al (2007)
13	Mango kernel activated carbon	7.83	Rai et al (2016)
14	Grafted banana peel	6.17	Ali et al (2016)

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15	Natural Akadama clay	4.29	Zhao et al (2013)
16	Coconut tree sawdust	3.6	Selvi et al (2001)
17	Activated carbon (UCS-DDAB)	3.46	Karnjanakom & Maneechakr (2019)
18	Rice straw	3.15	Hui et al (2008)
19	magnetically modified multi-wall carbon nanotubes	2.94	Bayazit & Kerkez (2014)
20	Spent activated clay	1.42	Weng et al (2008)

## CONCLUSION

Adsorbent dosage, contact time, pH, temperature, and initial metal ion concentration were the bases for a comparative analysis of all four adsorbents. For Cr, the optimal dose and contact time were found to be between 5.0 and 10 g L<sup>-1</sup> and 160 and 180 minutes, whereas for Pb, they were between 3.5 and 5.0 g L<sup>-1</sup> and 140 and 180 minutes. For all of the chosen parameters, the decreasing order of removal efficiencies was BB, OBB, LPB, and SLPB. The surface charges and mobility of the ions are key components of adsorption and are influenced by pH and temperature. According to SLPB, the highest removal of Cr and Pb was 95.47 and 97.42% at pH 3 and 5 and 65 and 55 oC, respectively. Additionally, all of the selected adsorbents had the lowest removal efficiency when initial metal concentration was included, which may be because this component depends on the dosage and duration of interaction with the adsorbent. Additionally, pH was the most crucial factor that controlled the removal process, and SLPB was the greatest adsorbent for the job.

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