



## Removal of mercury (II) from aqueous solution using bamboo leaf powder: Equilibrium, thermodynamic and kinetic studies

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### ABSTRACT

In this work the performances of unmodified bamboo leaf powder (BLP), modified by using anionic surfactant SDS (BLPS) and non-ionic surfactant Triton X-100 (BLPT) were evaluated for the removal of hazardous mercury (II) ions from water. BLP were characterized by BET and FTIR analysis. Detailed experimental investigations were carried out to find the effect of contact time, initial pH, adsorbent dose, agitation speed and temperature on the adsorption capabilities of unmodified and modified BLP. Adsorption isotherm, kinetics, thermodynamics and mechanism were also investigated to get insights of the adsorption. Experimental results showed that BLP can be used as an effective adsorbent for the removal of mercury (II) ions from the aqueous solutions. The maximum adsorption capacity was 27.11, 28.1 and 31.05 mg/g for unmodified, Triton X-100 modified and SDS modified BLP, respectively.

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### Introduction

Mercury and its derivatives are considered as priority pollutants due to their neurological toxicity, volatility, persistence, and bioaccumulation through food chain, which pose a great threat to both human health and organism security [1]. The main anthropogenic path way through which Hg (II) enters the water bodies is through wastes from industrial processes like chloralkali, paper and pulp, oil refinery, mining, electroplating, paint, pharmaceutical and battery manufacturing [2]. Therefore, environmental remediation for mercury (II) pollution has been considered to be one of the most important aims for environmental scientists and engineers. Among several chemical and physical methods, adsorption process is one of the effective techniques that have been successfully employed for mercury removal from wastewater [3–7]. Among the several types of adsorbents used for removal of metal ions from effluents, various types of biosorbents (materials of biological origin) have been strongly recommended by researcher for the removal of copper [8], cadmium [8], chromium [9], iron [10], manganese [10], selenium [11] and arsenic [12] from aqueous solutions. The main advantages of this technique are the low operating cost, improved selectivity for specific metal, removal of heavy metals from effluent irrespective of toxicity and short operation time. However, for industrial application, the selection of adsorbent material is mostly done by availability of waste material and applicability of the adsorption

method taking into account on space, cost, and the amount of wastewater.

Considering all these factors, the objective of the present work was to prepare an efficient adsorbent from bamboo leaves (bamboo leaf is abundant and is available in all parts of world in free of cost) and to investigate its potential application for the adsorption of Hg (II) from aqueous medium. Contrary to different reported literatures, the novelty of this work was enhanced by performing surfactant mediated surface modification of bamboo leaves (modified by anionic surfactant SDS and non-ionic surfactant Triton X-100) based adsorbent and comparing the adsorption performance. The prepared adsorbent was characterized by BET surface area measurement, SEM analysis and FTIR analysis. Effects of various operating parameters such as; initial mercury (II) concentration, contact time, adsorbent dose, initial pH, stirring and temperature were studied to observe their effects on the mercury (II) adsorption process. The Langmuir, Freundlich and Temkin isotherm models were used to describe equilibrium isotherms. The biosorption mechanisms of mercury (II) onto bamboo leaf powder were also evaluated in terms of thermodynamics and kinetics of adsorption. Efforts have been given to find the most probable adsorption mechanism of mercury (II) on bamboo leaf powder.

### Experimental

#### Materials and instruments

All reagents used in this work were of analytical grade and were used without further purification. Ingredients included Sodium

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hydroxide (Titan Biotech Limited, Rajasthan, India), Sodium dodecyl sulphate (Sigma–Aldrich), Triton X-100 (Sigma–Aldrich), Mercuric chloride (Fine Chemicals, Mumbai, India). A digital pH meter (Century Instruments, Chandigarh, India) was used to measure the pH of the solution. The concentration of mercury (II) was determined by atomic absorption spectroscopy (AAS). A mechanical stirrer (Type-RQ-126-D, Remi Motors Ltd., Mumbai) of impeller length 7 cm was used for stirring the solution. Fourier transform infrared spectrometry (Thermo-Nicolet FTIR, Nicolet IR-200, USA) was used to analyze the organic functional groups of the adsorbent.

#### Preparation and characterization of adsorbents

The mature bamboo leaf was collected from a bamboo garden which is very close to IIT Guwahati campus. The leaves were thoroughly washed with tap water to remove dust and other impurities and dried at 343 K in hot air oven overnight. Dried leaves were then ground, screened, washed two times with tap water to free the lignin part of the bamboo leaf and then dried under sunlight for 24 h. Dried bamboo leaf powder was kept in an airtight container for further use. For surface modification, 2 g of dried bamboo leaf powder was taken in 1 L beaker containing 500 ml of Sodium dodecyl sulphate (SDS) solution at its CMC level ( $8.10 \text{ mol/m}^3$ ) and another 2 g of bamboo leaf powder was taken in separate 1 L beaker containing 500 ml of Triton X-100 solution at its CMC level ( $0.20 \text{ mol/m}^3$ ). Both the beaker was stirred for 24 h at RPM 200 and at room temperature. It was filtered without further washing by distilled water and then dried for 24 h under sunlight. Finally, it was kept in air tight container. The amount of surfactant adsorbed on the surface of BLP was calculated as  $3.5 \text{ m mol/g}$  and  $0.1 \text{ m mol/g}$  for SDS and TX-100 modified BLP, respectively. The point of zero charge (pHZPC) of BLP, BLPS and BLPT was determined by using a solid weight to liquid volume ratio of 1:2. For this 100 mg of bamboo leaf powder was added to 200 ml of distilled water with varying pH from 2.2 to 8.6 and stirred for 24 h. Final pH of the solution was plotted against initial pH of the solution and shown in Fig. 1. pHZPC of BLP, BLPS and BLPT bamboo leaf powder was determined as 6, 6.1 and 6.6 respectively. Fig. 2 shows the FTIR analysis for bamboo leaf powder used for the adsorption experiments. The figure showed the presence of a large number of functional groups, notably  $-\text{NH}_2$  ( $3397 \text{ cm}^{-1}$ ),  $-\text{OH}$  ( $2920 \text{ cm}^{-1}$ ),  $-\text{C}=\text{O}$  ( $1645 \text{ cm}^{-1}$ ). Other peaks are due to the presence of organic framework and bending vibration of carbon-carbon double bond and carbon-oxygen double bond.

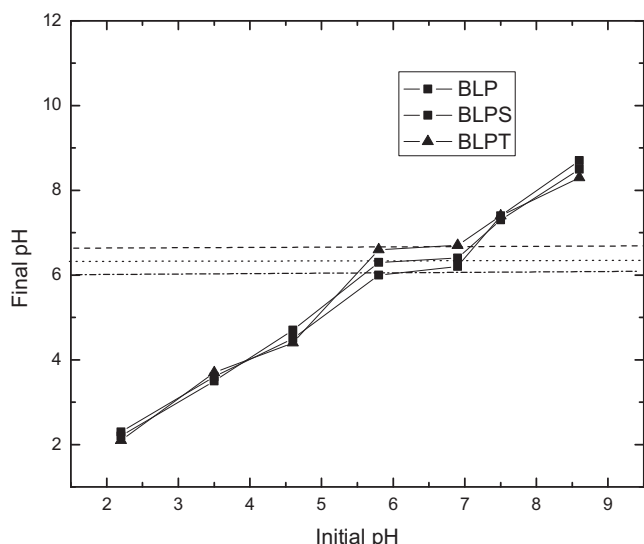


Fig. 1. Point of zero charge (pHZPC) of BLP used for the adsorption experiments.

#### Adsorption experiments

Mercury (II) solution (1000 mg/L) was prepared by dissolving 1.354 g of  $\text{HgCl}_2$  in 700 ml of distilled water. All the experiments were carried out by proper dilution of the stock solution and conducted at ambient temperature in winter ( $298 \pm 2 \text{ K}$ ) in batch mode using a 2 L beaker. Effects of contact time (10 min interval and upto 60 min), adsorbent dosage (1–8 gm/L), temperature (298, 308 and 318 K), initial solution pH (2–10) and stirring speed (100–1000 rpm) on the performance of Hg (II) adsorption over adsorption surface was investigated. The adsorption equilibrium experiment for mercury (II) solution was carried out by taking 100 ml of 100, 150, 200, 250 mg/L mercury (II) solution in 250 ml conical flask. The adsorbent dose was 400 mg, temperature was ( $298 \pm 2 \text{ K}$ ) and pH of 8. The whole system was agitated for 24 h (to confirm that the equilibrium has been reached) in mechanical incubator. After 24 h the solution attains equilibrium and the amount of mercury (II) adsorbed (mg/g) on the surface of the adsorbent was determined by the difference of the two concentrations. Triplicate experiments were carried out for all the operating variables studied and only the average values are taken into consideration. The average deviation of triplicate results in the units of concentration is found to vary as  $\pm 2\%$ .

A glass column of 90 cm length and 5 cm internal diameter was used as the fixed bed adsorber. The adsorbent bed was supported by glass wool and glass beads that ensure uniform liquid distribution. The bed was thoroughly rinsed with distilled water and left overnight to ensure a closely packed arrangement of adsorbent particles without voids, channels or cracks. The mercury (II) solution was fed through the bed in the down flow mode. A peristaltic pump was used to control the flow rate at the inlet and outlet. Samples were collected periodically and analyzed for the remaining mercury (II) concentration. The flow through the column was continued until the mercury (II) concentration of the column effluent approaches  $>98\%$  of the feed concentration. Blank experiments were carried out with mercury (II) solution and without adsorbent to ensure that no mercury (II) was adsorbed onto the walls of the beakers and agitator. The amount of mercury (II) adsorbed per unit weight of adsorbent at time ( $q_t$ ) and mercury (II) removal efficiency (R) was calculated as:

$$q_t = \frac{C_0 - C_t}{m} \times V \quad (1)$$

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where,  $C_0$  is the initial mercury (II) concentration (mg/L),  $C_t$  is the concentration of mercury (II) at any time  $t$ ,  $V$  is the volume of solution (L) and  $m$  is the mass of adsorbent (g).

## Results and discussion

#### Effect of contact time on mercury (II) adsorption

Fig. 3 shows the effect of contact time on the percentage adsorption of mercury (II) for unmodified and surfactant modified bamboo leaf powder. From the figure it is observed that, percentage adsorption of mercury (II) increases with time for both unmodified and surfactant modified bamboo leaf powder. Among three different adsorbents, SDS modified bamboo leaf powder shows maximum adsorption (80%) and unmodified bamboo leaf powder shows minimum adsorption (65%) whereas Triton X-100 modified bamboo leaf powder shows 76% adsorption after 60 min of adsorption. No improvement in mercury (II) adsorption was observed. The mercury (II) adsorption rate at the initial stage (first 50 min) may be explained by an increased availability in the number of active binding sites on the

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