Life Science Informatics Publications
Research Journal of Life Sciences, Bioinformatics, Pharmaceutical and Chemical Sciences
Journal Home page http://www.rjlbpcs.com/
RJLBPCS
ISSN 2454-6348

Original Research Article **DOI: 10.26479/2018.0403.20**

ADSORPTION FOR ENVIRONMENTAL REMEDIATION: MODIFICATION OF COMMERCIAL ACTIVATED CARBON FOR THE REMOVAL OF THALLIUM (I) AND BORON METAL IONS FROM AQUEOUS MEDIA

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ABSTRACT: This research study explore the study of Commercial Activated Carbon (CAC) modified using liquid-phase oxidation (by HNO_3) and heat treatment in an inert atmosphere (N_2) in the removal of two metal pollutants Thallium (I) & Boron metal ions by batch adsorption process from aqueous media. The process has been investigated as a function of pH [4 - 9 (Tl (I) & (B)], agitation time (5-80 minutes) and adsorbate concentration [(B: 1-20 & Tl(I): 2-100 mg/L)]. The experimental data was analyzed using equilibrium isotherm, kinetic and thermodynamic models. The single ion equilibrium adsorption data were fitted to two popular isotherm models Langmuir and Freundlich isotherm. The Langmuir model fit for the equilibrium data better than the Freundlich isotherm model in the studied initial metal concentration. The obtained R_L (separation factor) values were in the range of 0–1 indicating that Tl^{1+} and Boron adsorption were favorable. The kinetic data was tested using first, pseudo-second order models and intraparticle diffusion models. The results indicated that adsorption fitted well with the pseudo-second order kinetic model in adoption of both ions at room temperature.

KEYWORDS: Commercial Activated carbon, adsorption, characterization, Metal ion removal, Kinetics, Isotherm study.

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1. INTRODUCTION

In recent years, the need for safe and economical methods for the elimination of heavy metals from refinery waste waters necessitated research interest towards the production of low cost commercially available activated carbon. It has been increasingly used for the prevention of environmental pollution and antipollution laws have increased the sales of activated carbon for control of air and water pollution. Awareness of the water pollution has been a major concern for environmentalists worldwide. Various treatment technologies are applied to remove organic, Inorganic pollutants. Techniques used include adsorption, chemical reaction, filtration, ion-exchange, coagulation/flocculation, reverse osmosis, electrodialysis, and others . Among them adsorption process is found to be the most effective method for removing dissolved metal ions from wastes [1]. Thallium is a heavy metallic element that exists in the environment mainly combined with other elements (primarily oxygen, sulfur, and the halogens) in inorganic compounds. Thallium is quite stable in the environment, Compounds of thallium are generally soluble in water and the element is found primarily as the monovalent ion (Tl^{+}). Since thallium is a naturally-occurring element, it may be present in ambient waters in trace amounts and intake may cause harmful to human health. Thallium is considered a non-essential and highly toxic element, which is produced as a by-product in the refining of iron, cadmium and zinc [2]. The maximum contaminant levels of thallium in drinking water and wastewater (effluent) set by the United States Environmental Protection Agency (USEPA) are 2 and 140□g/l, respectively. The environmental safe dose of thallium for human is 1.7 μg/l [3]. High concentrations of the element boron in the water resources make them unusable for human consumption and for irrigation purposes. Recently boron has been classified as a pollutant of drinking water in national, EU and international drinking water directives. Concentrations of boron in drinking-water have wide ranges, depending on the source of the drinking-water, but for most of the world the range is judged to be between 0.1 and 0.3 mg/liter [19]. The mean daily intake of boron in the diet is judged to be near 1.2 mg/day.[20]. In the last two decades, several physico-chemical methods have been reported for removal of boron, but Adsorption is proved as cost effective process[12]. Comparatively little experimental work has been done relevant to this problem, with the exception of the studies conducted by amorphous aluminum and iron oxides, kaolinite, allophone [4], acid soils [5], pyrohyllite [6], hydrous ferric oxide [7], chitosan resin [8], activated carbon [9], fly ash [10], and clays and soils [11]. From the extensive literature study it was identified that Rivera-Utrilla *et al.* [12] studied the adsorption of Cs^{+1}, Tl^{+1}, Sr^{+2}, and Co^{+2} on activated carbons from aqueous solutions. They used three carbon types, e.g., two were produced from almond shells and one purchased from a commercial source. They also found that thallium was not removed when carbon was not present. The conclusion that the authors presented is that Tl^{+1} was adsorbed but then was oxidized to relatively insoluble thallium hydroxide or oxide. Sheya

and Palmer [13] investigated the effect of metal impurities (including thallous ions) on adsorption of gold by activated carbon (coconut) in cyanide solutions over the pH range 6.4-12.5. Rauws and Canton [14] suggest that potassium ferricyano ferrate (prussian blue) absorbs thallium ions almost quantitatively. Srivastava et al. [15] investigated the use of chromium ferrocyanide gel for removal of heavy metals. They found that the gel had a great affinity for heavy metals, including thallium.

Commercial grades of activated carbon are assignated as either gas-phase or liquid phase adsorbents. Liquid-phase carbons, generally in the form of powdered or granular, are characterized as having larger pores because of the need for rapid diffusion in the liquid decolorizing activated carbon are usually employed as powdered. Activated carbon is quite easy to manufacture, but much more difficult to adapt to specific applications. Physical forces are not always sufficient for total adsorption of a particular component. Specialty impregnated carbon refers to an activated carbon that is chemically coated or treated to enhance its adsorptivity towards specific compounds [16].

The present study is focused on modifying commercial activated carbon (Purchased from Chemical suppliers) by using nitric acid chemical treatment. The characterization of modified commercial activated carbon (CAC) was conducted by using several instruments including Scanning Electron Microscope (SEM)-Energy dispersive spectroscopy (EDX), Fourier Transform Infrared (FTIR) Spectroscopy. Low temperature nitrogen adsorption isotherms were used to estimate the BET surface area and pore size.

2. MATERIALS AND METHODS

All chemicals used in this study were of an analytical grade.

Adsorbate Solutions: Tl (I) stock solution with proper concentration (500 mg/L) was prepared by dissolving 0.163g of its nitrate (TlNO3, Merck, Germany) in double distilled water (pH 7.01). The boric acid solutions used in this study were obtained synthetically in the lab using deionized water and boric acid (AR Quality 99.8%, Merck). Standard boron stock solution in concentration of 1000 mg/l was prepared by dissolving 5.716 g of boric acid in 800 ml deionised water and diluting the sample to 1000 ml. Then, samples of 100 ml in 250 ml beaker were prepared by diluting the stock solution to various concentrations of boric acid solutions in order to be used for the experiments.

Adsorbent preparation: In this experiment, The CAC sample is of LR quality was purchased from Ranbaxy laboratories India Ltd., (Product No. CO 155). It is coconut shell based AC in granular form. The 100gm of CAC is transferred into a conical flask filled with 0.5N Nitric acid boiled for 60 minutes, filtered and washed with several times with double distilled water and dried in an Air oven at 102°C for several hours. After that, the material was placed in closed stainless steel vessels by maintaining inert conditions and pyrolysis was carried out in inert atmosphere at 400oC for 30 minutes followed by next stage to develop the pore size structure so that an accessible internal surface could be created. The product was finally dried and sieved to get 70 microns particle size.

The percentage of yield can be obtained by taking initial mass of the impregnated sample divided by the final mass of sample at the end of activation process.

2.1 Adsorbent characterization

2.1.1 Determination of surface area by BET method: BET-N2 adsorption experiments were carried out manometrically using an Autosorb (Quantachrome Crop.). All samples were degassed overnight at 200oC, prior to the adsorption experiments. The BET-N2 surface area was obtained by applying the BET equation to the adsorption data.

2.1.2 FTIR analysis: The adsorbents are examined using Fourier Transform Infrared spectroscopy (FTIR). The sample discs were prepared by mixing of 1 mg of powdered carbon with 500 mg of KBr (Merck; for spectroscopy) in an agate mortar, then pressing the resulting mixture successively under a pressure of 5 tones/cm2 for about 5 minutes., and at 10 tones/cm2 for 5 min., under vacuum. The spectra were measured from 4000 to 400 cm-1 on a NICOLET 670 model FTIR.

2.1.3 Scanning electron microscopy (SEM): The scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the microstructure morphology and chemical composition characterizations. The microphotograph of CAC sample before adsorption was recorded using LEO 1420 VP Compact variable pressure Digital SEM, manufacture by Leo Electron Microscopy Ltd. (Beam voltage 500 to 2000V, Magnifications 250 to 65,000 X, Resolution 3nm at 1000V).

2.1.4 Energy Dispersive x ray Spectroscopy (EDX): Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique used for the elemental analysis to identify the elements and their relative proportions (Atomic %) in a sample. Each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum and it was recorded for CAC before and after adsorption using BRUKER EDX Two-dimensional V ANTEC-500 detector.

2.2 Batch adsorption studies

The effect of various parameters on the removal of Tl (I) and Boron metal ions onto CAC was studied. For each experimental run, 100 ml of metal ions solutions of 5 mg/L initial Boron concentration and 50 mg/L Tl(I) solution, taken in a 250 ml plugged beaker. A suitable adsorbent dose (5 g/L) of CAC was added to conical flasks containing 100 ml metal ions solutions, adsorption of metal ions was carried out at room temperature 30±1◦C for 30 minutes in batch system on agitator (Remi Shaker) and the mixture was shaken at a constant agitation speed (500rpm) for 30 min. . Then, solution was filtered through Whatman No- 42 filter paper. The Tl(I)/Boron ion concentration in the sample after adsorption was determined using Atomic Adsorption Spectroscopy (Elico--Model). The same procedure has been adopted for the experiments carried out by varying parameters viz., (i) initial pH of the standard metal ions solutions (ranging from pH 4 to pH 9) (ii) agitation time (ranging from 5-80 minutes), and (iii) initial concentration of the standard metal ion

solution (ranging from 1.0 to 20 mg/L for Boron and 2.0 to 100.0 mg/L for Tl(I) ion).

The percentage removal of metal ion and amount adsorbed (in mg/g) were calculated using the following relationships:

Percentage removal (%R)= $(Ci - Ce)/Ci$ ×100…….(1)

Amount adsorbed (qe)= $(Ci - Ce)/m$ ……..(2)

Where Ci and Ce are the initial and final concentrations (in mg/L) of metal ion respectively and m is the mass of carbon (in mg/L). The average values of duplicate runs were obtained and analyzed. Error in data was found to be: ±0.5–1 % for percentage removal, ± 0.002–0.02 mg/g for amount adsorbed.

3. RESULTS AND DISCUSSION

The adsorption of Thallium (I) and Boron metal ions in aqueous solution on CAC were examined by optimizing various physicochemical parameters such as pH, amount of adsorbent and adsorbate initial concentration. Analysis of adsorption data is important for developing equilibrium isotherm equations that can be used for design purposes. The Powdered CAC obtained from Merck Company is the byproduct of wood based carbon with the characteristics S_{BET}=600m^2/g, total pore volume 0.82 cm^3/g and has micropores d ≤ 2.5 nm and mesopores 2 < d ≥ 30 nm diameters. After modification with nitric acid treatment S_{BET} raises to 900 m^2/g total pore volume 1.64 cm^3/g and has micropores d ≤ 2.8 nm and mesopores 2 < d ≥ 50 nm diameters. The development may be expected due to open the new pores (micro and meso) during the oxidation process. Tl (I) adsorption onto CAC, the surface area decreases to 756 m^2/g and 798 m^2/g in boron adsorption process. The decrease in surface are may be due to occupying the metal ions onto the pores of CAC.

3.1 FTIR analysis: FTIR spectroscopy in the range of 400 cm^{-1} to 4000 cm^{-1} was used to identify the functional groups on the activated carbon surface. The results of before and after adsorption are presented in Figure 1. The simultaneous presence of band in the regions 3616–3300 (cm^1) is due to -OH stretching of hydroxyl groups of CAC (Fig. 1). -CH_2 stretching is obtained at 2914 (cm^{-1}) and -C=O (carbonyl groups) stretching of resin is obtained at 1761 (cm^{-1}). Likewise, band observed at 650 (cm^{-1}) is due to metal oxygen stretching. The bands at 1444 and 1521 cm^{-1} are related to -C-C- stretching of aromatic ring stretching. The band at 417-540 cm^{-1} matches up metal oxygen vibrational mode. These bands were sharp and of strong intensity thus indicating the high degree of crystallinity of the samples. After adsorption all these bands are existed with slight intensity change in the peak area suggesting that the process may be physisorption.

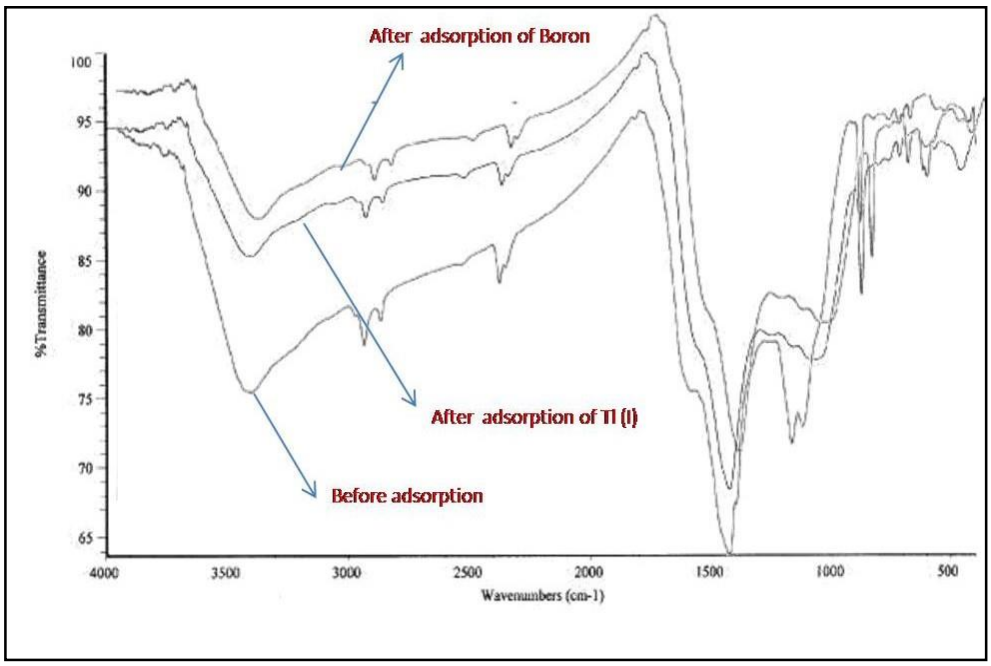
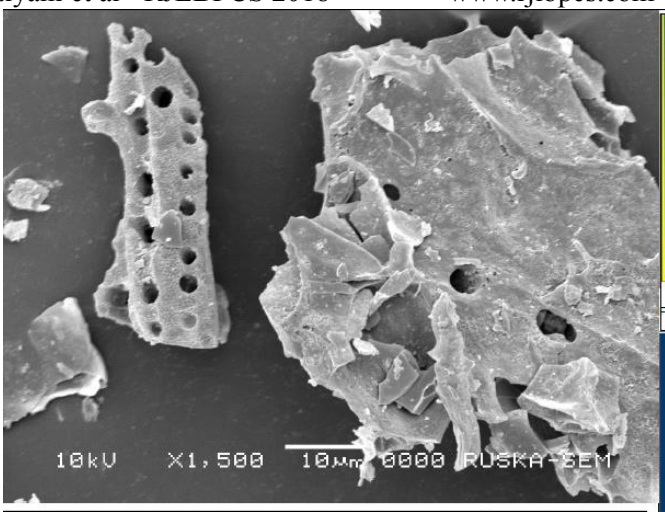
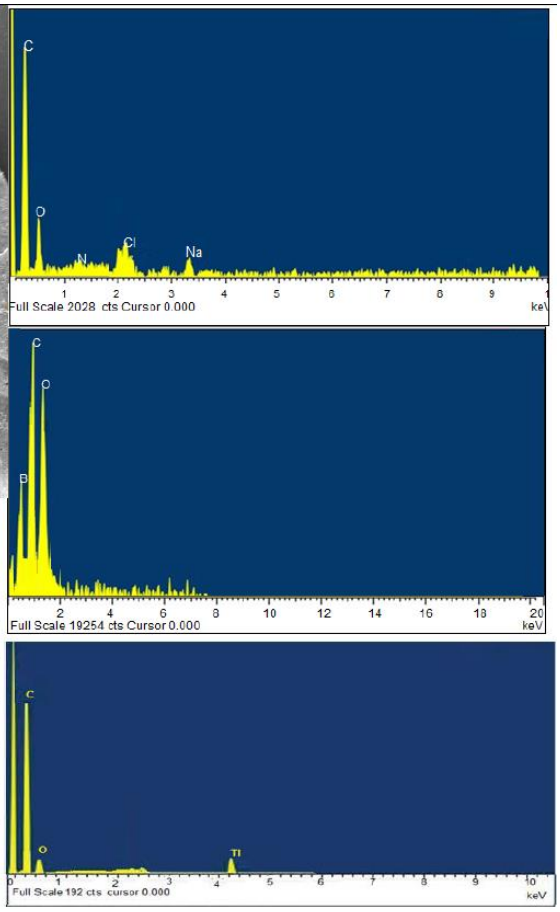


Figure 1: FT IR spectra of Commercial activated carbon before and after adsorption of Tl(I) and Boron

3.2 SEM-EDX analysis:

SEM-EDX photographs of CAC shown in Figure 1 reveal the surface texture, porosity of the sample and its chemical composition before (SEM only) and after adsorption. The availability of pores and internal surface is requisite for an effective adsorbent. The SEM images (Figure 2) of the adsorbent and the Tl(l) ion & B ions loaded adsorbent indicated the presence of coverage of Tl(l) & B ions (element confirmed by EDX analysis) over the adsorbent material. SEM micrographs of the activated carbon gives a clear picture of the porosity of an adsorbent and also shows complex disorganized surface structures of different open pore sizes and shapes. EDX data was presented Fig. 2 on comparing the spectrum of samples taken and after adsorption process, a small peak pertains to Tl(l) & B could be noted with the sample after adsorption process. The EDX elemental analysis highlighted the presence of carbon, oxygen, Nitrogen, Sodium and Chloride ions in before adsorption and Tl(l) & Boron elements appeared in treated sample. EDX detected the emission of elements of carbon (C), oxygen (O), Nitrogen (N), Sodium (Na) and chlorine (Cl) in untreated samples and Thallium & Boron in treated sample, the percentage (wt%) of all elements was investigated and its concentration before and after treatment also given in figure 2.





Element (Series)	Before adsorption		After Adsorption of Tl(I)		After Adsorption of Boron	
	Wt (%)	At(%)	Wt (%)	At(%)	Wt (%)	At(%)
C (Kα)	64.24	55.67	70.01	80.57	78.67	77.67
O (Kα)	29.04	33.61	29.102	17.64	20.3	19.37
Cl (Kα)	4.35	6.681	0	0	0	0
Na (Kα)	1.67	2.67	0	0	0	0
N (Kα)	0.7	1.37	0	0	0	0
Tl (Kα)	0	0	0.945	1.79	0	0
B(Kα)	0	0	0	0	1.03	1.97

Figure 2: The SEM-EDX spectra of CAC before (SEM) and after adsorption (EDX) of Tl (I) and Boron

3.3 Effect of pH

In general the adsorption of Tl (I) and Boron ion depends on the pH, solid composition, surface site concentration, adsorbate nature and concentration, and formation of solution complex, along with ionic strength and competing adsorbate ions. The studies regarding the pH dependence on Tl (I) and Boron adsorption on CAC shows (Figure 3) that the Tl (I) and Boron ions adsorption is a function of pH. The effect of pH on the adsorption of Tl (I) and Boron on CAC has been studied in the pH range 4-9 at room temperature (30±1°C) at fixed initial adsorption concentration (50 mg/L). Results indicate that metal adsorption depend strongly with pH and increased with increasing pH up to 6 later it was decreases. This increase in metal ions removal with pH may be due to the decrease in electrostatic repulsion between cations and the positively charged surface of CAC at pH > pH_{PZC} (pH_{PZC}=8.9). Below pHpzc, the surface is positively charged under these conditions the uptake of metal ions would be quite low due to electrostatic repulsion, beyond pHpzc the negative charge on the surface of adsorbent increase thereby enhancing the metal adsorption. For all experiments, pH 7 was chosen as the optimum solution pH. Above that precipitation may observed.

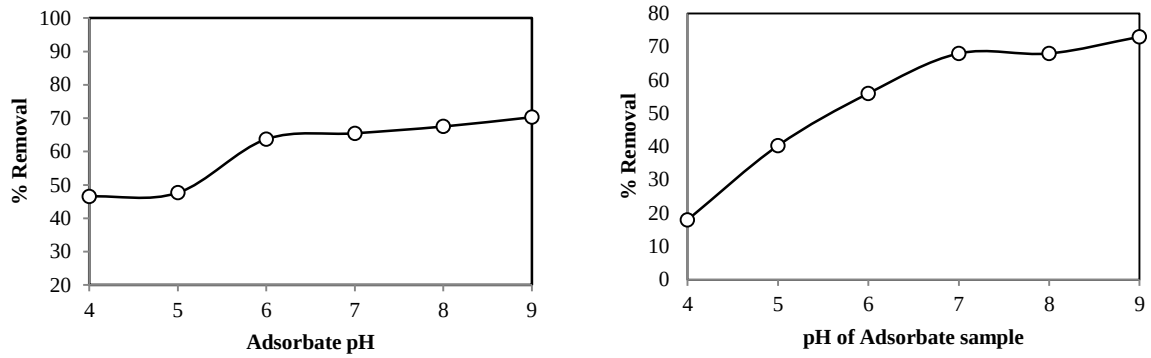


Figure 3: Effect of initial pH on % removal of Thallium (I) (Left) and Boron (Right) removal

The amount of Tl(I) and B ion removed from solution increased with an increase in the pH range of 4-7 after which it leveled off and become constant (Fig. 3). At pH values less than 4, the acidic functional groups become protonated and thus are no longer available to attract metal ions from solution. When the pH is greater than 7, the acidic groups are de-protonated and therefore negatively charged and able to bind the positively charged thallium ions.

3.4 Effect of Initial Concentration

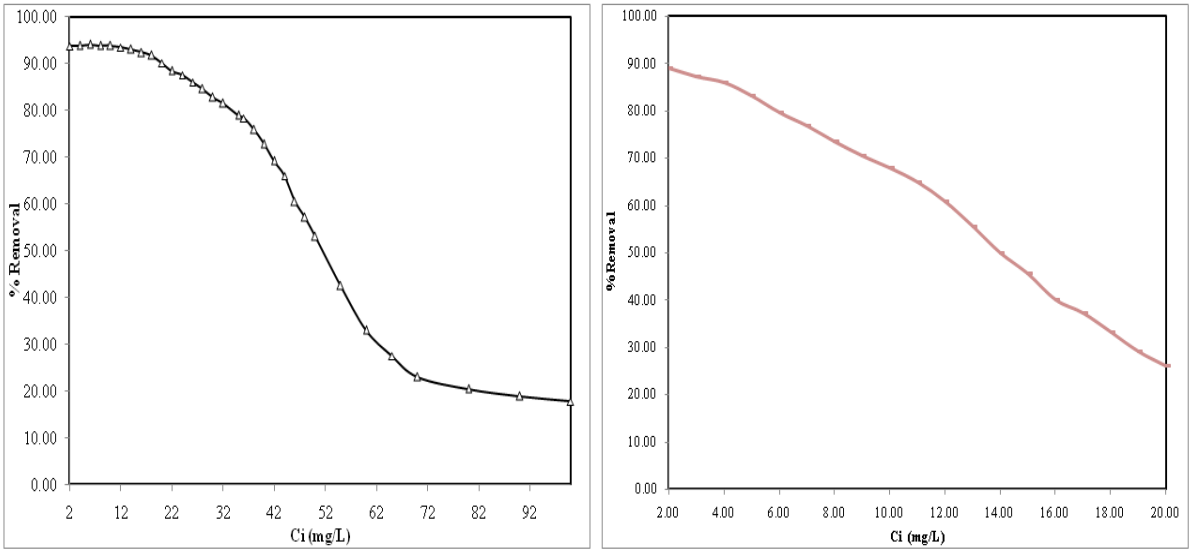


Figure 4: Effect of Initial Concentration on % removal of Thallium (I) (Left) and Boron (Right) removal

3.5 Adsorption Isotherms

Adsorption isotherm considers a relationship between adsorption capacity and concentration of the remaining adsorbate at constant temperature [21]. Langmuir and Freundlich adsorption isotherm models are employed in this study to describe the experimental adsorption isotherm. Langmuir adsorption is based on the fact that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface [22, 23]. The linear form of the Langmuir equation can be represented by Bouhamed F et al., [24]

$$\frac{C_e}{q_e} = \frac{1}{b}Q_0 + \frac{C_e}{Q_0}$$

Where qe is the amount of metal ion adsorbed (mg/g) and Ce is the equilibrium concentration of metal ion in the bulk solution (mg/L) while Qo is the monolayer adsorption capacity (mg/g) and b is the Langmuir constant related to energy adsorption capacity. The constants Qo and b can be calculated from slope and intercept of the plot 1/Ce Vs 1/qe . Freundlich isotherm is an empirical equation describing the heterogeneous adsorption and assumes that different sites with several adsorption energies are involved [25]. The linear form of the Freundlich equation is shown below.

$$\log qe = \log k + \frac{1}{n} \log Ce$$

The slope 1/n gives adsorption capacity and intercept log K gives adsorption intensity from straight portion of the linear plot obtained by plotting log qe versus log Ce .

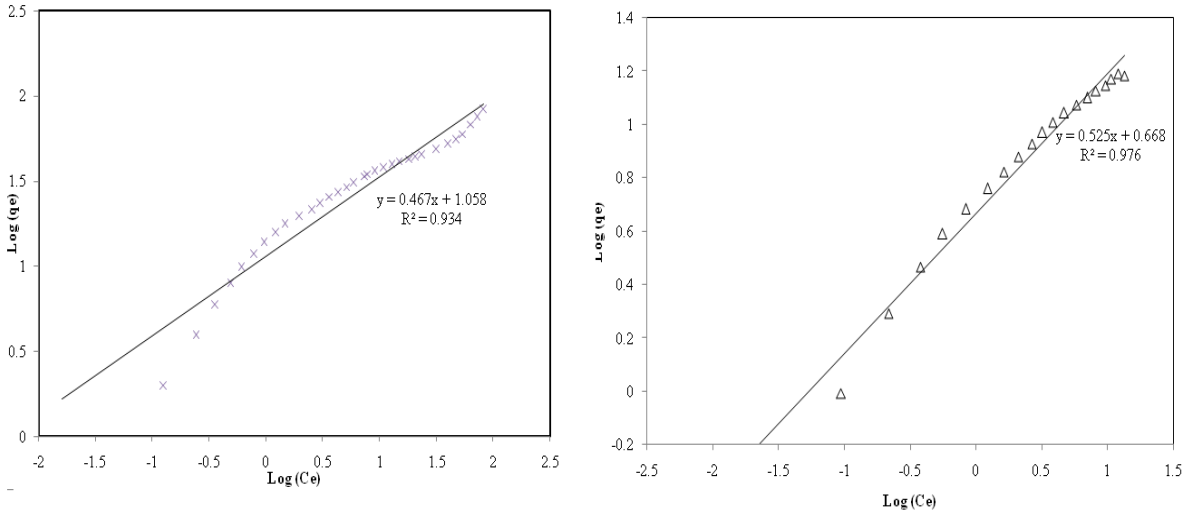


Figure 5: Freundlich adsorption isotherms for the removal Tl (I) and Boron

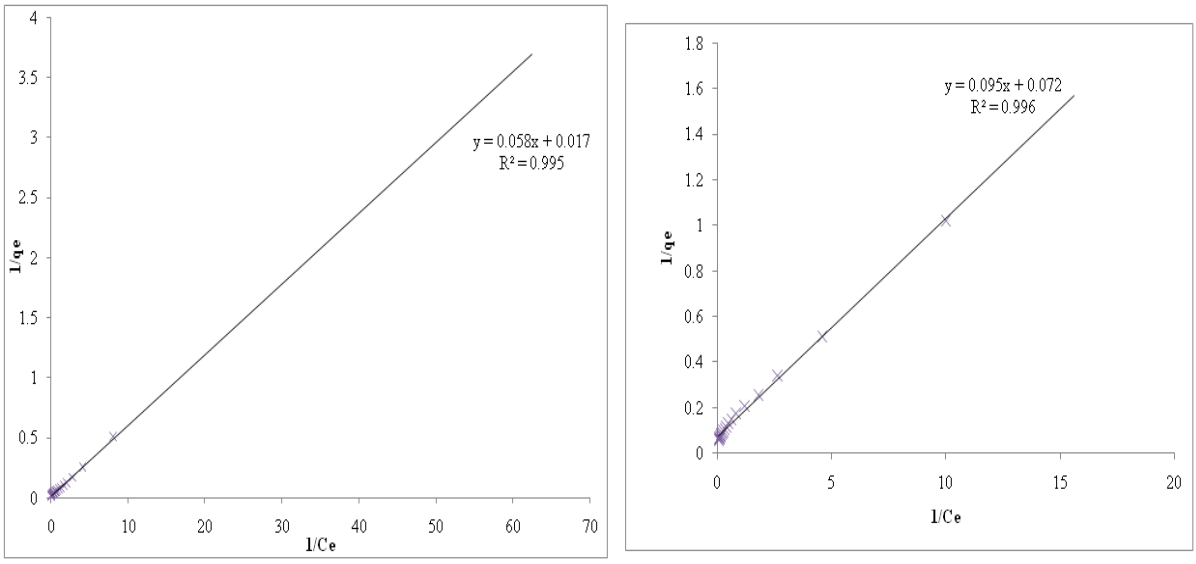


Figure 6: Langmuir adsorption isotherms for the removal Tl (I) and Boron

Three models of adsorption isotherm namely Langmuir & Frendulich were applied for the adsorbents under study, and the results obtained gave a high correlation values in the adsorption process are 0.995 & 0.996 for Tl (I) and Boron adsorption respectively. Langmuir graphs (Fig.6) showed almost linearity (evidences by r values 0.99) among the adsorption points in the straight line equation as compared to Freundlich (Fig.5) thus Langmuir model is fit for the present adsorption process.

3.6 Effect of adsorbent dose

The effect of varying doses of CAC was investigated using 50 mg/L of initial Tl (I) and 5mg/L Boron concentration at optimum conditions. The removal of metal ion was found to increase with an increase in adsorbent dosage from 0.5 g/L to 5 g/L later adsorption capacity is minimum in both the cases. Figure 7 shows an increase in percentage removal of Tl (I) and Boron ions with the increase in dose of adsorbent up to a certain limit (4- 5 g/L) and then it remains almost constant. Increase in the adsorption with increasing dose of adsorbent is expected due to the increase in adsorbent surface area and the availability of more adsorption sites [26]

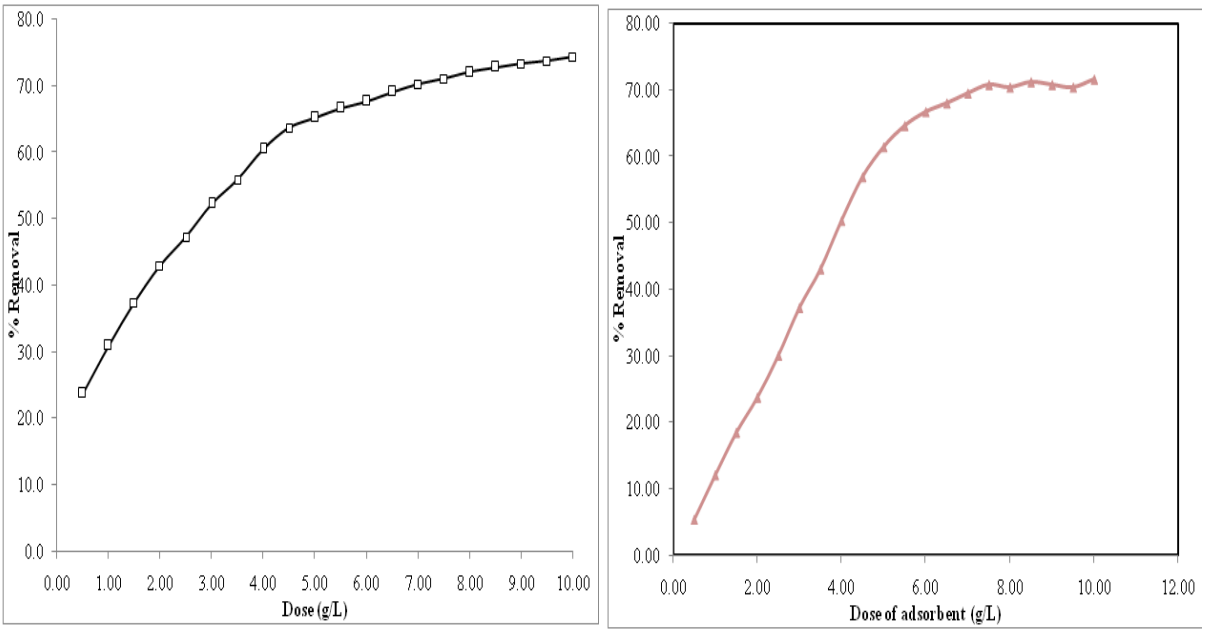


Figure 7: Effect of Dose on % removal of Thallium (I) (Left) and Boron (Right) removal

3.7 Effect of agitation Time

The effect of contact time was correlated for the adsorption of Tl & B ions at regular time intervals ranging from 5 to 80 min. Figure 8 revealed that the % removal increased and became constant after 35 to 40 min. The maximum adsorption capacity of 88 % for B & 85 % for Tl ions removal was observed at 40 min.

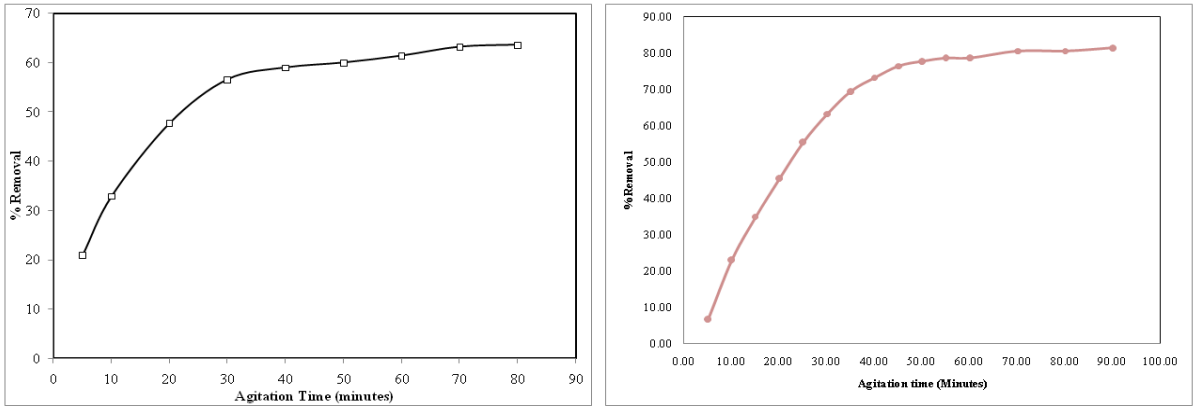


Figure 8: Effect of agitation time on % removal of Thallium (I) (Left) and Boron (Right) removal

The removal rate was slow within the first 25-30 min then increases rapidly and gradually diminished to attain equilibrium within 40 min beyond which there was no significant increase in the removal rate. It is thought that the first step leads to surface adsorption and the second step leads to intraparticle transport from bulk fluid to the external surface of the porous adsorbent [27]. This trend agrees with the report of other investigators [28]. The stages of sorption of Tl & B ions on activated carbon might be controlled by the diffusion process from bulk to the surface or the heterogeneous nature of the adsorbent.

3.8 Kinetic study

Frequently used kinetic models (Viz; Pseudo – first order, Largergren's first order, intra-particle diffusion and the Pseudo-second order kinetic model) have been tested to investigate the adsorption mechanism of Tl(I) and B^+ on CAC.

The pseudo-first-order kinetic model is shown by the following equation [29]:

$$\ln q_e - q_t = \ln q_e - k_1 t$$

where q_e and q_t (mg/g) are the amount of adsorbate adsorbed at equilibrium and at any time, (minutes), k_1 min^{-1} respectively, and (1/minutes) is the adsorption rate constant. Figure 9 shows that the linear plot of ln $(q_e - q_t)$ versus time (minutes) gives a gradient of k_1 and intercept at ln q_e .

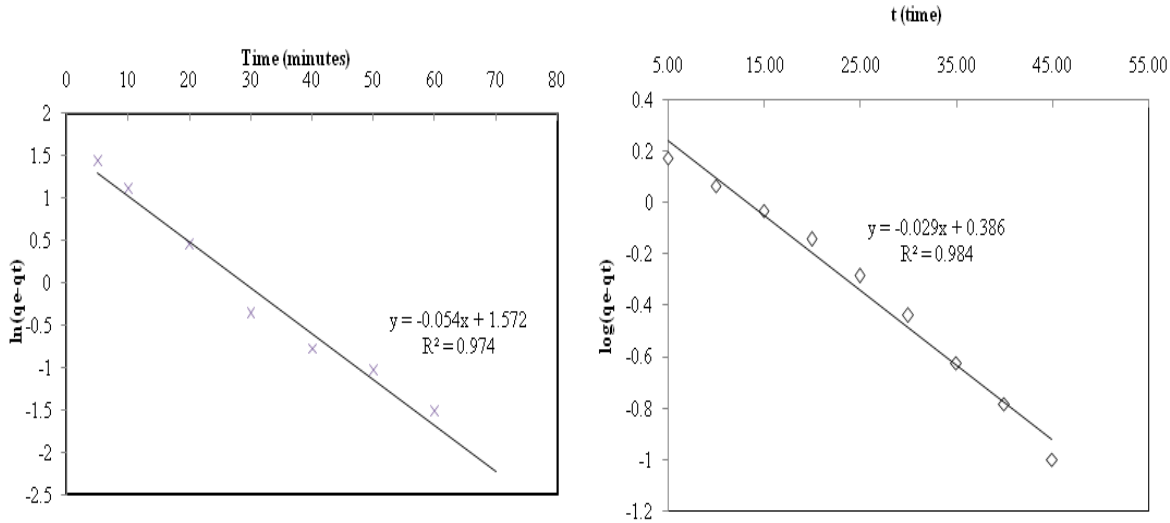


Figure 9: The linear plots pseudo-first-order model (Lagergren) for the adsorption of Tl(I) and B onto CAC sample

The pseudo second-order model predicts the performance over the total range adsorption and is expressed as [30]:

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

The linearized-integrated form of the equation is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e}$$

where k_2 (mg/g. min) is the rate constant of second-order adsorption. Figure 10 shows that the linear plot of t versus $\frac{t}{q_e}$. Generally, the pseudo second-order model is proper to the adsorption kinetics.

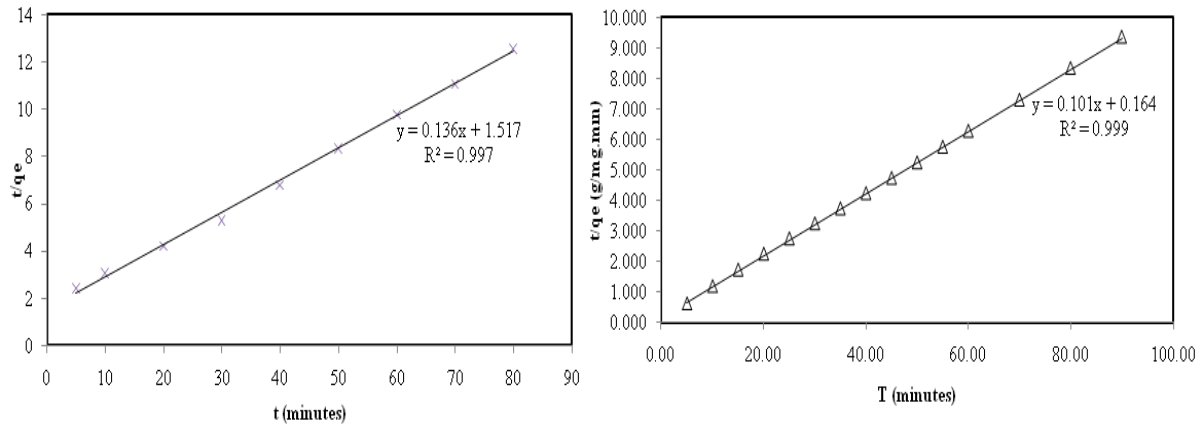


Figure 10 : The linear plots pseudo-second-order model for the adsorption of Tl(I) and B onto CAC sample

The straight lines plots showed a good agreement of experimental data with pseudo-second-order model and pseudo first order model. Comparing the R^2 values (0.997 & 0.999) for both ions adsorption process), pseudo-second-order and Lagergren model show a significant agreement with adsorption mechanisms being the two, with successfulness of the pseudo-second-order model

3.9 Intra – Particle diffusion model

The possibility of intra-particle diffusion process was explored by using the Weber and Morris intra-particle diffusion model [31]

$$q_t = k_{id} t^{1/2} + C$$

q_t = amount of metal ions adsorbed at time t (mg/g), C = intercept, k_{id} = intra particle diffusion rate constant (mg/g $min^{-1/2}$). The r-values are found to be close to unity, indicating the application of this model. The calculated values of k_{id} for the two systems were maximum for Tl(I) (0.015) and minimum for B (0.0087). The intra particle diffusion plots are given in Figure 11. The values of intercept (I) give an idea about the boundary layer thickness i.e. the larger the intercept, the grater is the boundary layer effect [31]. I values were maximum in Tl(I) (0.8694) and minimum in B (0.8591) indicating that the boundary layer effect is maximum in Tl(I) and minimum in Boron.

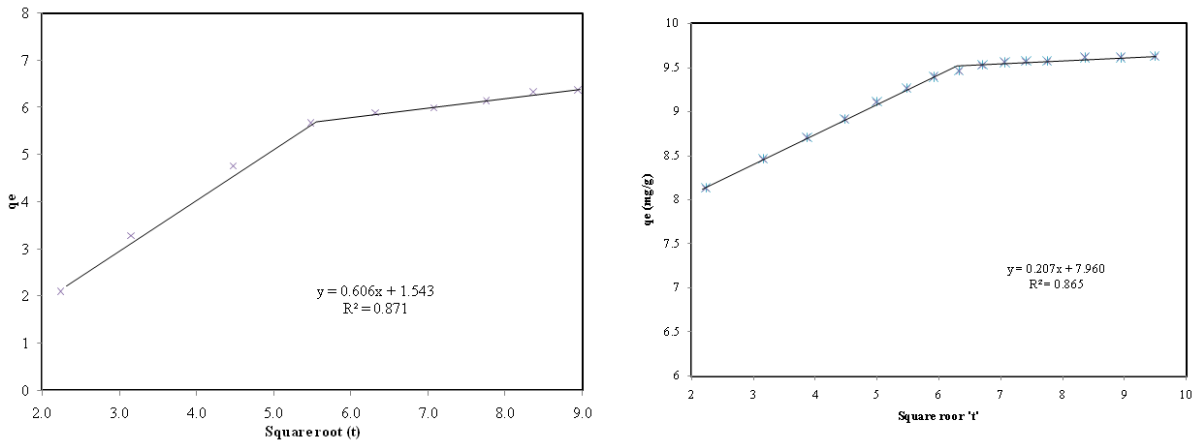


Figure 11: Plots of Intra particle diffusion model for the adsorption of Tl(I) and B onto CAC sample

4. CONCLUSION

The SEM-EDX analysis indicated that the concentration and distribution of elements were different prior to and after Tl & B adsorption in the CAC. The IR spectroscopy demonstrated the slight variation in IR spectra of the sample prior to and after confirms the physisorption process. SEM, and BET confirmed that the pores of the activated carbon are mostly in range of mesopores to macropores. The mechanism of Tl(I) and Boron adsorption onto CAC was found to be based on the

assumption of intra-particle diffusion, controlled Pseudo second order mechanism with physisorption being the predominant mechanism. A short contact time necessary to reach equilibrium indicates that the predominant mechanism is physisorptions. The adsorptions of metal ions are pH dependent. It was noted that ionic radius of metal ion has an influence in the magnitude of metal loading on the adsorbent.

5. CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

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