International Journal of Engineering Science Invention (IJESI)
ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726
www.ijesi.org || PP. 29-36

Adsorption Studies Of Mixed Activated Carbons In The Removal Of Thallium (I) ION From Aqueous Media

Ch.S.R.G.Kalyani[1]*, Dr K.Surendra Babu[2], Dr. Medikondu Kishore[3]
1PhD Research Scholar & Asst Professor, 2Research Supervisor & Director (PG Studies), 3Professor
Department of Chemistry, SVRM College (Autonomous), Nagaram
**Author for Correspondence: chsrgk@gmail.com*

Abstract: *The synthesis and characterization of activated carbons (ACs) obtained from lignocellulosic precursors is a topic widely studied by a number of researchers worldwide. In the last decades, an increase has been observed in the number of publications related to the synthesis, modification, characterization and application of ACs obtained from lignocellulosic materials. Particularly, the applications of these carbons are primarily focused in the removal of several inorganic and organic pollutants from water and wastewaters. There are several locally existing materials that can be used for the removal of heavy metals. Low cost adsorbents such as natural materials, agricultural wastes etc are found to be more encouraging in heavy metal removal due to economical, metal selective, regenerative and are highly effective. In this context, the present research work explore the development of two chemically modified activated carbons form Agricultural based byproducts (Tamarindus Indica Stem Carbon, Ocimum Sanctum bio mass carbon) and the tested their feasibility for Thallium ion removal from aqueous solution. Batch experiments were performed to test effects of adsorbent dosage, contact time, initial Thallium concentration solution pH, and coexisting anions on metal removal. . The results showed that the adsorption percentage depends on the conditions and the process is strongly pH-dependent. On the basis of kinetic and isotherm studies, the data was better fitted to the pseudo-second order kinetic model and Langmuir Isotherm. The satisfactory adsorption percentage of Tl(I) ions, 84.7%, obtained at 30 ± 1°C. The equilibrium data agreed fairly better with Langmuir isotherm than Freundlich isotherm.*
KEYWORDS - 50:50 ratios of Activated carbons, Tamarindus Indica Stem Carbon, Ocimum Sanctum bio mass carbon, Bath adsorption, Thallium Removal, Isotherm study and Kinetics

I. Introduction

The preparation of activated carbons (ACs) has been the subject of extensive research study for many years due to the diversity of their applications. Mainly though, activated carbons have been used as adsorbents and catalysts. Carbonized wood, which can be regarded as a crude form of activated carbon by present-day standards, has been in use for many thousands of years and activated carbons from agricultural byproducts, waste materials are used in a number of industrial applications including separation and purification technologies, catalytic processes, biomedical engineering, and energy storage, among others. The extensive application of activated carbon is mainly due to its relatively low-cost with respect to other adsorbents, wide availability, high performance in adsorption processes, surface reactivity [1]. Traditionally, the activated carbons used in wastewater treatment are obtained from coal/lignite, wood or plant bio mass but, recently, there is a growing interest in the use of alternative and low-cost precursors for their production. Specifically, lignocellulosic wastes are a low-cost natural carbon source for the synthesis of several materials including the production of activated carbons [2]. The high cost of commercial activated carbons, estimated as more than 3.0 US$/Kg [3], stimulates in fact the development of effective low cost adsorbents for the removal of metals from wastewater [4].

The utilization of agricultural by-products for removal of heavy metals from solutions is gaining much attention these days. The toxic nature of heavy metals necessitates the design and synthesis of novel adsorbents for their effective removal from the environment. Selective adsorption has become important in recognition, sensing, and separation of molecules and ions. An adsorbent with a high adsorption capacity and a good selectivity is very critical in adsorptive separation.

The presence of heavy metals in the environment poses a problem due to their harmful effects on human health. Thallium (Tl) is considered a non-essential and highly toxic element, which is produced as a by-product in the refining of iron, cadmium and zinc [5]. It occurs almost exclusively in natural waters as monovalent thallium (Tl^{+1}). Thallium appears in two oxidation states; Tl (I) which is highly soluble in aqueous environments and resembles alkali metals and Tl (III) which is more stable forming complexes with sulphates, chlorides, carbonates and nitrates The solubility of thallous compounds (e.g., thallous hydroxide) is relatively high so that Tl^{+1} ion is readily transported through aqueous routes into the environment. The major sources of thallium are the base metal sulfides and precious metal bearing sulfides. Therefore, it has been shown to be a contaminant constituent in waters emanating from heavy metal sulfide bearing deposits. The maximum contaminant levels of thallium in drinking water and wastewater (effluent) set by the United States Environmental Protection Agency (USEPA) are 2 and 140μg/l, respectively. The environmental safe dose of thallium for human is 1.7 μg/l [10]

II. Literature Survey

A large number of investigations have focused on surface adsorption as a means of removing metals like Se, As, Pb etc from aqueous phase solutions, e.g., adsorption on ferric hydroxides, aluminum hydroxides, alumina, activated carbon, clays, etc. However, much less has been published concerning thallium removal by adsorption. From the extensive literature study it was identified that Rivera-Utrilla *et al.* [6] 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 [7] 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 [8] suggest that potassium ferricyano ferrate (prussian blue) absorbs thallium ions almost quantitatively. Srivastava et al. [9] 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.

In this study, activated carbons were prepared from *Tamarindus Indica* Stem (wood) and *Ocimum Sanctum* bio mass, activated with nitric acid, suitable for removing heavy metal ion Tl^{+1} from aqueous media. Equilibrium and kinetic models were used to estimate the sorption potential and the rate of reaction respectively. The overall goal of this research was to characterize TIC+OSC (50:50) combined adsorbent sample in order to establish an economical and environmental friendly method for the removal and pre-concentration of thallium from aqueous matrices. The potential benefit of this study is to provide a certain theoretical basis for operational design and applicable practice of the sorption systems of Thallium (I) metals removal, which has drawn increasing attention in the area of water environmental protection.

III. Experimental

All chemicals used were of analytical grade and obtained from Merck/Sd Fine chemical Ltd. India.

Apparatus

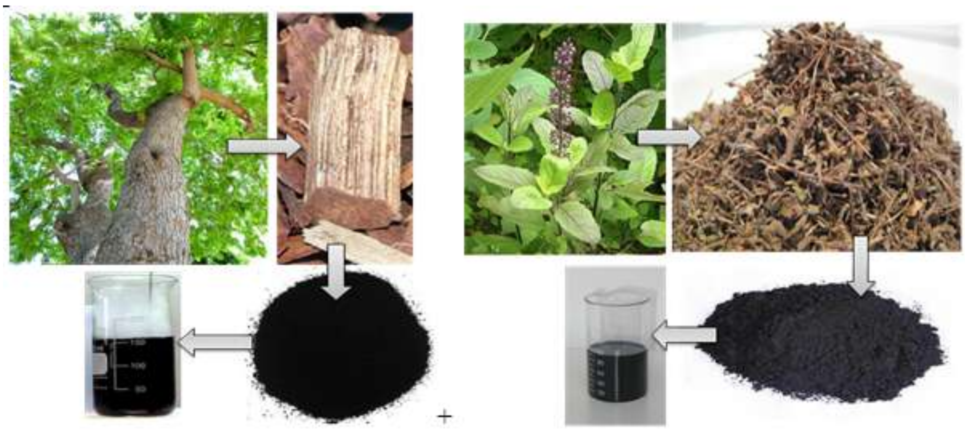
Atomic absorption spectrophotometer (AA220 Model, VARIAN Co., USA) and a pH meter (420A Model, ORION Co., USA) were used for measuring the concentration of Tl(I) ions and pH of solutions respectively.

Adsorbent Preparation

The adsorbent for the removal of Thallium (I), from ground water samples was prepared from the wood of *Tamarindus Indica* Stem wood. The wood (60 x 25 cm) was collected and dried naturally. It was then cut into small pieces and strongly heated in open air, cooled and then pulverized using a ball mill and sieved using a standard sieves to obtain the adsorbent of 75μ particle size (Figure 1). This carbons sample is indicated as (TIC) in further discussion. In the same way 500g of dried bio mass (except root part) of *Ocimum Sanctum* collected from agricultural field carbonized as in Tamarindus Carbon preparation (Figure 1). This carbons sample is indicated as (OSC) in further discussion. 5g of each carbon (separately) was stirred with 0.5 M HNO_3 solution for 30 min at 200 rpm at 100^oC on magnetic stirrer for 2 hours (Remi Made). The acid treated carbon was filtered, washed with 1% $NaHCO_3$ and washed with hot double distilled water for several times. Later, the suspension was decanted, washed with distilled water until filtrate get 7 pH and then kept in an oven at 110°C up to 6 h for complete drying. Obtained carbon samples are mixed in equal weights (50:50) used as adsorbent material in the Present adsorption study for the removal of Tl(I) ion from aqueous media.

Adsorbate Solution

Tl (I) stock solution with proper concentration (500 mg/L) was prepared by dissolving 0.163g of its nitrate ($TlNO_3$, Merck, Germany) in double distilled water (pH 7.01). All chemicals used in this study were of an analytical grade.



Tamarindus Indica Stem Carbon (TIC) + *Ocimum Sanctum* bio mass carbon (OSC)

Figure 1: Pictorial representation of the process involved in the derivation of activated carbon

Batch adsorption Process for the removal of Tl (I) ion

50 ml of standard Tl(I) ion solution (10 mg/L) was pipette out into a 250 ml beaker. To it, mixed amount of 100 mg (50mg of TIC + 50 mg of OSC) of the prepared active carbon was added and stirred at 200 rpm mechanically for 30 minutes. Then, solution was filtered through Whatman No- 42 filter paper. The Tl(I) ion concentration in the sample after adsorption was determined using AAS. The same procedure has been adopted for the experiments carried out by varying parameters viz., (i) initial pH of the standard Tl(I) ion solution (ranging from pH 2 to pH 9) (ii) agitation time (ranging from 5-90 min), and (iii) initial concentration of the standard Tl(I) solution (ranging from 1.0 to 15 mg/L).

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

Percentage removal $(\%R) = \frac{C_i - C_e}{C_i} \times 100$…………….(1)

Amount adsorbed (q_e)= $\frac{(C_i - C_e)}{m}$………………….(2)

Where C_i and C_e are the initial and final concentrations (in mg/L) of Tl(I) 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.

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 microphotographs of AC (TIC+OSC) sample before and after adsorption were 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).

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 AC Sample (TIC+OSC) before and after adsorption using BRUKER EDX Two-dimensional V ANTEC-500 detector

IV. Results And Discussion

SEM-EDX analysis: The SEM Photo Graphs have been studied for information about the surface features such as pore characteristics, shape and size of the particles making up the surface of carbons, the elements that the activated carbon is composed of and the relative amounts of these and how the atoms are arranged in the activated carbon sample.

The SEM images (Figure 2) of the adsorbent and the Tl(l) ion loaded adsorbent indicated the presence of coverage of Tl(l) ions (element confirmed by EDX analysis) over the adsorbent material. The examination of the SEM micrographs of the magnification micro pores was clearly identifiable. EDX data was presented Fig. 2. On comparing the spectrum of samples taken and after adsorption process, a small peak pertains to Tl(l) could be noted with the sample after adsorption process. The EDX elemental analysis highlighted the presence of carbon and oxygen ions in untreated and Tl(l) ion treated samples. The intensity of the Tl(l) signals was higher in samples treated with Tl(l) and was below the limit of detection on the untreated samples.

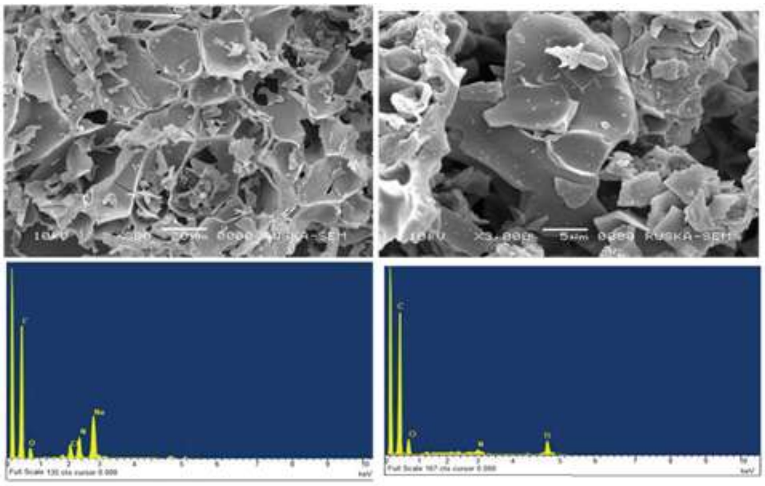


Figure 2: The SEM-EDX spectra of before and after adsorption onto AC (TIC+OSC) sample

The effect of solution initial pH on adsorption percentage

The solution initial pH is the major parameter controlling sorption processes. Tl (I) uptake as a function of hydrogen ion concentration (pH) was determined for pH values from 2 to 10. pH effects at equilibrium are presented in Figure 3. As seen in Figure 3, Tl(I) sorption on to AC sample is increased from pH=2 to pH=5 and then it is drastically decreased by increasing pH. The satisfactory Tl(I) sorption occurred at pH=5. In general, results indicated that the adsorption is highly pH dependant. Similar results have been reported in literature [11].

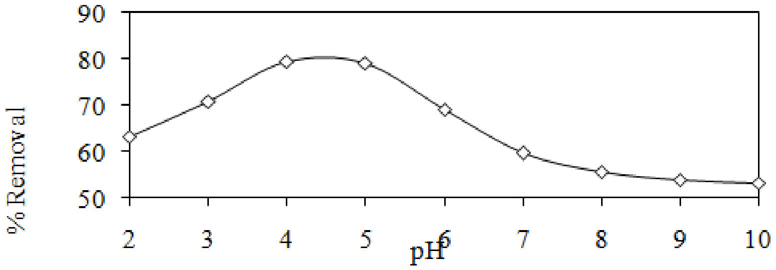


Figure 4: Effect of Thallium ion solution pH onto AC (TIC+OSC) sample

(Initial concentration, 10 mg/L; adsorbent dosage, 3 g/L; contact time, 30 min and temperature =30±1^{o}C)
pH values affect species of heavy metals in aqueous solutions and heavy metals removal increases as pH value rises, reaching a maximum around 5.0. Solution pH also makes effects on the adsorbent and the surface charge of the AC samples changes. This means that the removal of Tl (I) ions from the solution also contributes to the pH modification. However, at low initial pH values, below 4, the influence of adsorption is the only effect responsible for the reducing of pH Tl (I) ions in the solution. This suggests that the process is a suitable application on heavy metals removal because of its neutral and clean effluent.

Effect of Initial Concentration

The metal ion adsorption capacities of AC sample was presented as a function of equilibrium concentration (5–100 mg/L) in aqueous solution in Fig. 4 .All other Parameters such as contact time (30 min) and quantity of sorbents (3g/L) and pH 5 were kept constant. The metal uptake mechanism is particularly dependent on the initial Tl(I) concentration (Ci). At low concentrations metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and the exchange sites are filled. Sorbent exhibited very high metal loading capacities for this metal ion 45.8 mg/g for Tl (I) for AC Sample. This is due to the increment in the driving force produced from the concentration gradient [12].

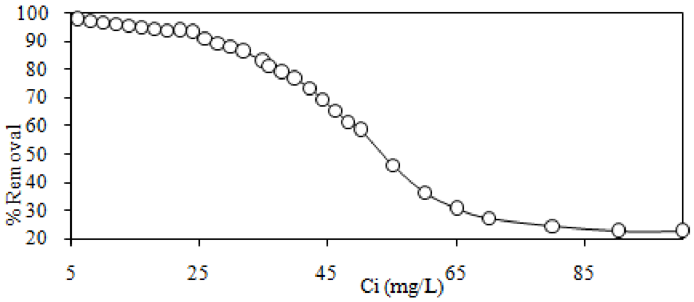


Fig 5: The effect of initial concentration of Tl (I) ion on its adsorption percentage removal, pH 5; contact time, 30 min; adsorbent dosage, 3.0 g/L and temperature =30±1°C.

Effect of Stirring Time

In the adsorption system contact time place a vital role, irrespective of the other experimental parameters that effect the adsorption kinetics. In order to study the kinetics and dynamics of adsorption of fluoride by various adsorbents, the adsorption experiments are conducted and the extent of removal of fluoride is conducted by varying the contact time (range: 5-100 min) at optimum conditions.The effect of contact time on Tl (I) ion adsorption is shown in Figure 7.

The percentage Tl (I) ion removal at different time was worked out using equation 1 and a plot was prepared between the percentage fluoride removal and contact time Figure 6. It can be noted that the percentage fluoride removal is increasing with time and attained almost an equilibrium condition (at which the rate of adsorption of solute is equal to the rate of desorption). In about 30-40 minutes the decreasing removal rate, particularly towards the end indicates a possible monolayer of Tl (I) ion on the outer interface of the carbon and pore (Intraparticle) diffusion onto the inner surface of the adsorbent particles through the film due to continuous agitatation maintained during the experiments. The data also indicate the removal of Tl (I) ion by these adsorbent samples is rapid at the initial period but becomes slow and almost stagnates with the increase in the contact time. The relative increase in the extent of removal of Tl (I) ion is substantially low after 30 min of contact time and it is negligible after 60 min by the adsorbent sample, which is fixed as the optimum contact time. This indicates that the rate of removal of Tl (I) ion is higher in the initial stage due to the availability of adequate surface area of the adsorbent. With increase in contact time and due to the decrease in the availability of active sites the adsorption process decreases. Though equilibrium of the adsorption process was found to be attained in about 30 minutes, the particle contact time for the adsorption process under the condition chosen may be taken as 30 minutes as most of the Tl (I) ions are absorbed by adsorbent sample.

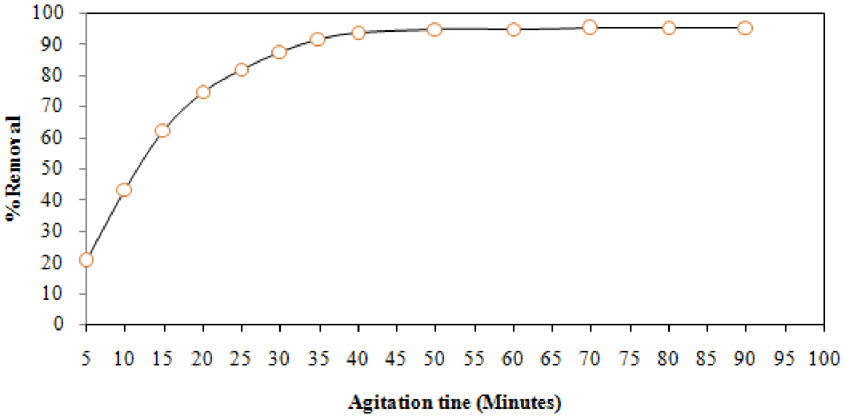


Fig 6: The effect of Stirring time of Tl (I) ion on its adsorption percentage removal

Adsorption isotherms studies

This study was carried out to establish the relationship between the concentration of Tl(I) ions and its degree of adsorption onto the surface of the AC adsorbent sample at a fixed temperature. The adsorption isotherm constants obtained from the plots of the linearized Langmuir and Freundlich models from Figure 7 & Figure 8. The Freundlich and Langmuir expressions for the removal of Tl(I) ions by TIC+OSC carbons sample are shown in Eqn. 3 and Eqn. 4, respectively.

Linear form of Freundlich isotherm equation:

:$Log\ (q_e) = \log K_f + (\frac{1}{n}) \log C_e$……………………….………. Eqn. 3

Linear form of the Langmuir isotherm˙
$Ce/qe = Ce/q_m + 1/Kaq_m$ ……….. Eqn. 4

From Figure 8 it can be seen that coefficients of determination (R^2) for AC sample from the Langmuir isotherm model was found to be 0.972. This indicates that Langmuir isotherm model satisfactorily described the adsorption of Tl(I) onto AC Sample. This indicates the monolayer coverage of Tl(I) ions on the homogenous surface of TIC+OSC carbons sample. The Langmuir equilibrium parameter R_L value for AC was found to be within the range for favorable adsorption ($0 < R_L < 1$) [13]. The maximum uptake capacity for AC sample was found to be 22.5 mg/g. This is better than some of the adsorption capacities for agricultural by-products reported in the literature. It can be seen that the Freundlich R^2 value from AC sample was found to be 0.672, (Figure 7). This indicates that the adsorption data was not sadequately described by Freundlich isotherm model. The adsorption intensity 1/n value for Tl(I) ions adsorption was found to be 0.4. This indicates a favorable adsorption process with increasing adsorption capacity and the appearance of new adsorption sites [14].

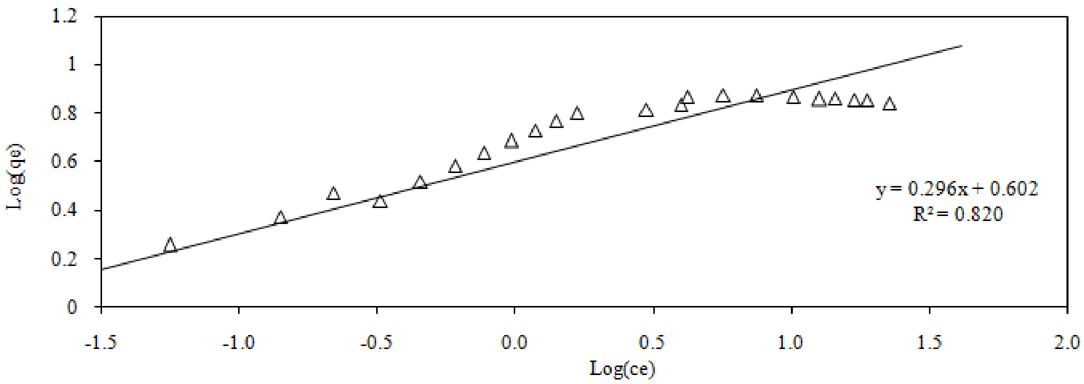


Figure 7. Freundlich Isotherm for Tl(I) ions removal

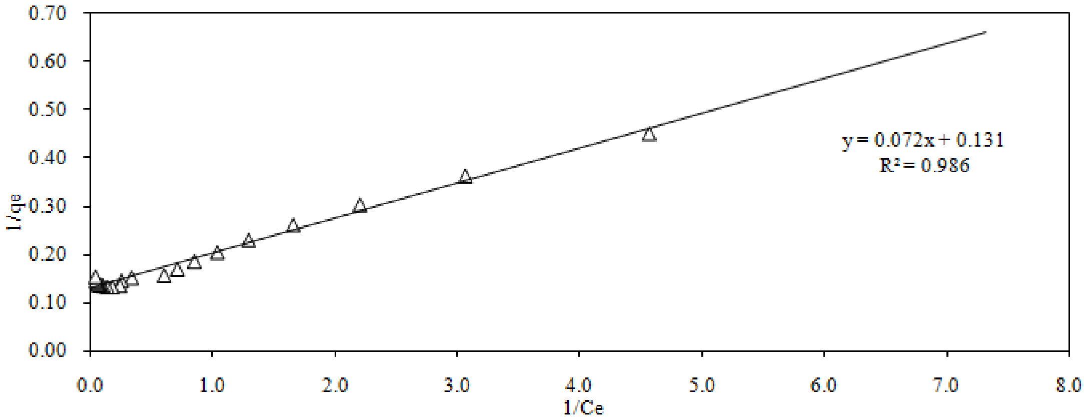


Figure 8. Langmuir isotherm for Tl(I) ions removal

Kinetics

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of F- ion removal was carried out to understand the behavior of prepared low cost carbon adsorbents**.**

Pseudo second order

The pseudo second-order adsorption kinetic rate equation is expressed as[15]

$\frac{t}{qt} = \frac{1}{K_2 q^2{}_e} + \frac{1}{qe}(t)$……….Eqn 5

The plot of (*t/qt*) and *t* of Eq. (5) should give a linear relationship from which *qe(1/slope)* and k_2*(slope²/Intercept)* can be determined from the slope and intercept of the plot, respectively. Available studies have shown that the pseudo-second order rate equation is a reasonably good fit of data over the entire fractional approach to equilibrium and therefore has been employed extensively in the study of adsorption kinetics.
However, it is not uncommon to observe multi linearity on *t/qe* Vs *t* plot (Fig 9). The trend is usually such that the rate constant decreases with time or more specifically decreases with increasing solid phase concentration.

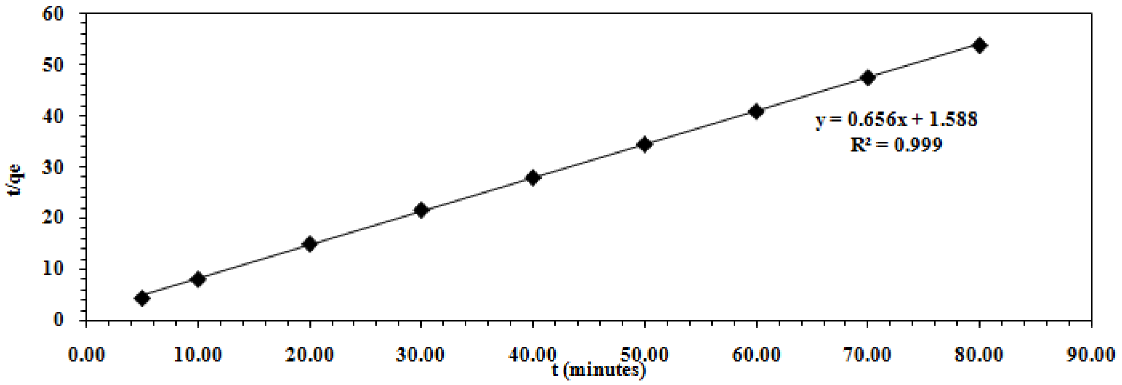


Figure 9: Pseudo-second-order kinetics for the adsorption of Tl (I) onto AC sample

In the present kinetic study we compare the R^2 values for the three adsorbent sample having 0.998 very close to unity hence pseudo-second order kinetic equation is fit for the AC adsorption study.

Intraparticle Diffusion Method

Intraparticle diffusion model assumes that the film diffusion is negligible and intraparticle diffusion is the only rate controlling step, which is usually true for well-mixed solutions. The intraparticle diffusion model is a single-resistance model in nature and can be derived from Fick’s second law under two assumptions.

The mathematical expression thus obtained for the intraparticle diffusion model is

$q_e \approx k_p t^{0.5}$...........(6)

Where k_p (mg/g $\text{min}^{-0.5}$) is defined as the intraparticle diffusion rate constant and is related to the intraparticle diffusivity in the following way

.$k_p = \frac{6q_e}{R}\sqrt{\frac{D}{\pi}}$...............(7)

Where R (cm) is the particle radius and qe (mg/g) is the solid phase concentration at equilibrium. The plot of the average particle loading, q_e(mg/g), versus the square root of time, $t^{0.5}$ (Figure 10), would yield a straight line passing through the origin if the adsorption process obeyed the intraparticle diffusion model. The slope of the straight line equals to k_p, the Intraparticle diffusion rate constant. This has resulted in linear relationship as evidenced by the r-values (0.814) for the current study which indicate the existence of intraparticle diffusion process.

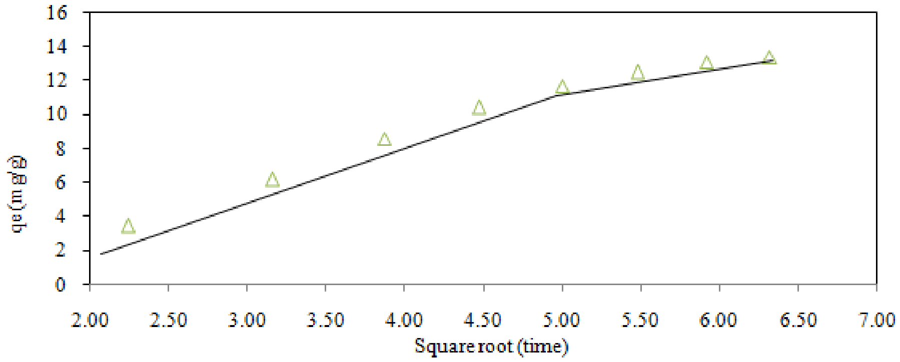


Figure 10: Intra particle diffusion plot for the removal of Tl (I) ion by the AC sample

When intra particle diffusion plots were observed (Figure 10) for the three AC sample the process was occurred in two stages. In the current adsorption system stage I one is observed in the square root ‘t’value 2.0 to 6.5. In this stage R^2 value was observed and confirm that for the current system close to unity but in the second stage i.e. above 6.5 (√t) were found to be 0. 849 for AC sample. So the current adsorption system strongly following the intraparticle diffusion process at initial stages compare to the final stage

V. Conclusions

The present study has shown that activated carbons mixed sample produced from *Tamarindus Indica* Stem Carbon, *Ocimum Sanctum* bio mass carbon, can be engaged as an environment friendly and low cost adsorbent for the removal of Thallium (I) ions from synthetic aqueous solution. The study on the effect of pH revealed that the competition between H+ and metal ions at low pH values is the main leading factors that affect the adsorption characteristics of AC sample. Optimum removal efficiency was achieved at pH 5.0. The number of adsorption sites increased due to an increase in AC dosage and optimum removal efficiency of 84.7% was achieved at AC sample dosage of 3 g/L.

References

[1]. Alam, M.Z., Ameem, E.S., Muyibi, S.A. & Kabbashi, N.A. (2009). The factors affecting the performance of activated carbon prepared from oil palm empty fruit bunches for adsorption of phenol. *Chemical Engineering Journal*, Vol. 155, No. 1-2: 191-198

[2]. Mohamed, A. R., Mohammadi, M. & Darzi, G.N. (2010). Preparation of carbon molecular sieve from lignocellulosic biomass: A review. *Renewable and Sustainable Energy Reviews*, Vol. 14, No. 6:1591-1599

[3]. Ahmaruzzaman, M., (2011). Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Advances in Colloid and Interface Science* Vol.166: 39-59

[4]. Velghe I., Carleer R., Yperman J., Schreurs S., D'Haen J., (2012). Characterization of adsorbents prepared by pyrolysis of sludge and sludge/disposal filter cake mix, *Water Research*, 46: 2783-2794

[5]. V. Zitko (1975), Toxicity and pollution potential of thallium, *Sci. Total Environ.* 4:185–192.

[6]. Rivera-Utrilla, J., Ferro-Garcia, M., (1984) Studies on the Adsorption of Cesium, Thallium, Strontium and Cobalt Radionuclides on Activated Carbons from Solutions. *J. Chem. Biotechnol.,* Vol. 34A:243-250

[7]. Sheya, S., Palmer, G., (1986) *Effect of Metal Impurities on Adsorption of Gold by Activated Carbon in Cyanide Solutions*. US Department of the Interior, RI 9268:page 11.

[8]. Rauws, A., Canton, J., (1976) Adsorption of Thallium Ions by Prussian Blue. *Bulletin of Environmental Contamination and Toxicology,* Vol. 15, No. 3, pp.335-336.

[9]. Srivastava, S., Bhattacharjee, G., (1980) Studies in the Use of Inorganic Gels in the Removal of Heavy Metals, *Water Research*. Vol. 14, No. 2:113-115.

[10]. MWTP (Mine Waste Treatment Program), *Issues identification and technology Prioritization Report. Thallium. Activity* 1, EPA, MWTP-143,MSE-TA, Butte, MT, USA, 1999, vol. 8, p. 76.

[11]. Wilson J A, Pulford I D and Thomas S S,(2003) *Environ Geochem Health*., 25(1), 51–56.

[12]. Sun G, Xu X (1997) Sunflower Stalks as Adsorbents for Color Removal from Textile Wastewater. *Industrial & Engineering Chemistry Research* 36: 808-812.

[13]. M. Rafatullah, O. Sulaiman, R. Hashim, and A. Ahmad, (2009) "Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust," *Journal of Hazardous Materials*, vol. 170, pp. 969-977

[14]. M. Hasnain Isa, L. Siew Lang, F. A. H. Asaari, H. A. Aziz, N. Azam Ramli, and J. P. A. Dhas,(2007) "Low cost removal of disperse dyes from aqueous solution using palm ash," *Dyes and Pigments*, vol. 74, pp. 446-453

[15]. Y.S. Ho, G. McKay, (1999) Pseudo-second order model for sorption processes, *Process Biochem.* 34 :451–4