

Reduction of COD and turbidity in leachates through coagulation-adsorption

Vivek Laishram^a and Potsangbam Albino Kumar^{b*}

^{a,b}Department of Civil Engineering, National Institute of Technology, Manipur-795004

*Email: albinoit@gmail.com

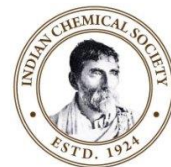
Abstract: In this study, aluminium sulphate, ferric chloride and polyaluminium chloride coagulants were employed for reduction of organic colloids through coagulation-flocculation and then adsorption using *Parkia Speciosa* (Petai) pods activated carbon for removal of dissolved ions from leachate. Polyaluminium chloride showed maximum turbidity reduction of 93.25% and 96.80% at optimum pH 4 for fresh and stabilized leachate respectively as compared to that of aluminium sulphate and ferric chloride with turbidity removals ranging from 70% to 91% for both types of leachate. The optimum doses of aluminium sulphate, ferric chloride and polyaluminium chloride for fresh leachate were 8 g/L with corresponding COD removals of 80%, 90% and 75% respectively. However, for stabilized leachate COD reduction, polyaluminium chloride and ferric chloride exhibits the same removals of 77.78% using 4 g/L and 3 g/L respectively against 55.55% by 4g/L aluminium sulphate. As the pre-treated effluents still have COD above the permissible limit, activated carbon derived from *Parkia Speciosa* pods was used as an adsorbent for further treatment. On the application of the diffusion model for fresh leachate, high R² values of 0.976 and 0.992 were observed using 10 g/L and 20 g/L adsorbent dose respectively resulting in overall COD removals of 85% and 89.50% respectively. For stabilized leachate, high R² values of 0.964 and 0.992 were observed for adsorbent doses of 5 g/L and 10 g/L respectively resulting in overall COD removals of 91.67% and 93.33% respectively, confirming the physical diffusion of organics in the adsorbent as the predominant mechanism rather than chemical adsorption.

Keywords: Leachate, Coagulation-flocculation, Adsorption, Activated Carbon, *Parkia Speciosa* (Petai).

Introduction

A major environmental pollution problem of municipal solid waste (MSW) landfill is landfill leachate. Leachate percolates through soils and sub-soils causing several environmental problems like potential contamination of surface and groundwater, if not collected separately, treated safely and well disposed. The composition of landfill leachate is very complex and it usually contains high concentrations of organic and inorganic pollutants, pathogenic microorganisms, ammonium-nitrogen, heavy metals that are very toxic to the surrounding soil, surface water and groundwater^{1,2}. Younger landfills generate fresh leachate with a high concentration of organics having higher biodegradability (BOD₅/COD>0.5). Fresh leachate from Thessaloniki landfill, Greece had COD concentrations as high as 70900 mg/L, with BOD₅ reaching up to 26800 mg/L³. Older landfills are more stabilized and generate lower concentrations of organics. Typical stabilized landfill leachate generally has moderate COD concentration ranging between 5000 mg/L and 20,000 mg/L, high ammonium nitrogen concentration ranging between 3000 mg/L

and 5000 mg/L, basic pH (~7.5) and low biodegradability (BOD₅/COD < 0.1)⁴. Landfill leachate treatments are categorized in the following three major sections: 1. Leachate treatment combined with domestic sewage treatment by a municipal wastewater treatment plant, 2. Leachate treatment by aerobic and anaerobic biodegradation processes (Biological methods), 3. Leachate treatment by physico-chemical methods¹. Biological treatments were very efficient in the removal of organic and nitrogenous matter in fresh leachate when the BOD₅ concentration is high and the BOD₅/COD ratio is more than 0.5^{1,5}. However, its efficiency is strongly limited in the presence of refractory compounds like fulvic acid and humic acid in landfill leachate. A high concentration of humic substances in leachate, representing 39% of the dissolved organic carbon and high nitrogen content was reported⁶. For the removal of refractory pollutants in leachate, many physico-chemical treatment methods like coagulation-flocculation, chemical precipitation, nanofiltration, adsorption and reverse osmosis were employed⁷. Among physico-chemical techniques, coagulation-



flocculation has been used in leachate pre-treatment prior to a biological or other physico-chemical process^{3,8}. In coagulation-flocculation, pH, coagulant dose and coagulant type play a very important role. The removal of COD, color, turbidity and humic acids were 56.38%, 63.38%, 89.79%, and 70.41% respectively at a polyferric sulfate dose of 8 g/L at pH 6.0⁹. 0.5 g/L aluminium sulphate, 0.7 g/L ferric chloride, 0.6 g/L polyaluminium chloride and 0.5 g/L polyferric sulfate at the optimum pH range of 5.5-6 resulted in suspended solid removals of 85%, 89%, 91%, 85%, turbidity removals of 92%, 93%, 99%, 94%, and COD removals of 49%, 65%, 61% and 62% respectively¹⁰. Coagulation-flocculation resulted in high turbidity removals due to the settlement of colloids by charge neutralization as well as sweep flocculation. However, certain drawbacks are moderate COD removal, sludge production and an increase in aluminum or iron concentration from coagulants^{3,11,12}.

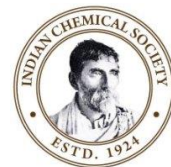
Adsorption, an alternative physico-chemical treatment method of water and wastewater is a better option because of its convenience, ease of operation and simplicity in design^{13,14}. The commonly used adsorbents are granular activated carbon and powdered activated carbon. The adsorption of pollutants on the surface of activated carbons greatly reduces the dissolved organic pollutants, mainly COD and heavy metals because of the large surface areas of the activated carbon, finely porous structure, rich functional groups and surface reactivity¹⁵. ZnCl₂-treated rice husk and sugarcane bagasse activated carbon resulted in removing phenol, COD, color of 80%, 70% and 60% respectively at 4 hr equilibrium time using 30 g/L of activated carbon¹⁶. However, the limitations of adsorption are the high consumption of activated carbon and the need for frequent activated carbon regeneration¹⁰. After biological or chemical treatments in wastewater treatment plants, adsorption treatments are done for dissolved organic and inorganic matter removal that remained from the previous biological and chemical treatments¹⁷. The combination of the coagulation and the adsorption processes may reduce the limitations of each single process. High removal of turbidity with fractional removal of COD which are incorporated with the

colloids and which are in settleable form can be achieved by coagulation-flocculation. This in turn lower the COD load for the following adsorption processes¹⁰. The coupling of the two treatment techniques, namely coagulation-flocculation and adsorption may be an effective combination for treatment of landfill leachate. This study aimed to examine the feasibility of the combined coagulation-flocculation and adsorption treatment processes for turbidity and dissolved organic matter mainly COD removal from leachate procured from Lamdeng landfill site located at Lamdeng Khunnou Solid Waste Management Plant, Manipur, India by the use of three coagulants aluminium sulphate, ferric chloride, polyaluminium chloride and powdered activated carbon adsorbent derived from *Parkia Speciosa* (Petai) pods.

Materials and methods

Sample collection and preparation

Landfill leachate was sampled once every two weeks from October 2018 to June 2019 from the sanitary landfill site of Lamdeng Khunnou Solid Waste Management Plant, Manipur, India. The solid waste management plant is located at Lamdeng in the Imphal-west district of Manipur state, India (24°84'24.7704" N, 93°53' 23.9244" E) and is situated 13 km away from the capital city, Imphal. The estimated solid waste generation in the state is 284.40 metric tonnes per day (TPD) and the actual waste collected accounts to 156.38 TPD. Out of the total waste collected, 110.50 TPD (70.6%) are processed daily by the waste processing unit in the plant¹⁸. The waste management plant has a sanitary landfill site accounting to around 45.88 TPD (29.4%)¹⁸. For the characterization and experimental works, the leachate was sampled and filled in 20 L clean polypropylene containers, brought to the laboratory and storing was done at 4°C in order to minimize the microbial activity that may change the leachate characteristics. The fresh leachate was sampled from the equalization tank which controls the outflow of raw leachates whereas stabilized leachate was sampled from the evaporation sump pond which was exposed to the atmosphere. pH and electrical conductivity were recorded by digital pH and electrical conductivity meter (PCS Testr 35: Eutech 01X441506/Oakton 35425-10) at the sampling



site. All the analyses in this study were conducted in triplicates until concordant values were obtained, and all the tests were carried out according to the standard methods¹⁹. The standard deviation values of all the experiments were within ± 5 . If the standard deviation >5 , the values were discarded and the experiments were performed again. In this study, activated carbon derived from *Parkia Speciosa* (Petai) pods was used for the removal of dissolved organic ions mainly COD from the pre-treated leachate. Petai pods contain an abundant amount of minerals and bioactive compounds like Phenol (51.9-84.24 mg Gallic acid equivalent (GAE/g), methanolic content of 5.28 mg retinol equivalent (RE)/g²⁰ and these compounds are known to have good binding properties with the dissolved ions in wastewater.

Synthesis of adsorbent

Pretreatment

After the procurement of dry *Parkia Speciosa* (Petai) beans from local markets, soaking was done for 12 hours in tap water to regain moisture after which the petai pods were manually removed from the seeds. The pods were then repeatedly rinsed with distilled water to remove residues and then dried at 100°C for 24 hours to reduce moisture content. The dried petai pods were then grounded using a commercial miller and sieved using a 300 μ sieve.

Impregnation

In this study, phosphoric acid was used as an activating agent for *Parkia Speciosa* pods. To obtain an impregnation mass ratio of 1:1, 100 g of the dried, ground and sieved pods were added into a conical flask containing 167 ml of 30% phosphoric acid. The conical flask was then shaken for about 5 minutes for homogeneity and left to impregnate for 24 hours. Activation was done to enhance the pores on the surface of activated carbon.

Carbonization

The phosphoric acid impregnated Petai pods were carbonized 3 times consecutively, each of 10 min carbonization time at 400°C. The sample was mixed thoroughly, each time after 10 min carbonization time to get a homogeneously carbonized activated carbon. After 30 min of carbonization, the activated carbon produced was then cooled and rinsed with distilled water repeatedly to obtain neutral pH and then dried

again at 100°C for 24 hours. The final activated carbon was then sieved using a 125 μ sieve and used for adsorption studies²¹. The maximum surface area and pore volume of the activated carbon measured using the Micromeritics 2020 surface analyser, were 184m²/g and 0.0872 cm³/g respectively obtained at 400°C carbonization temperature using an impregnation ratio of 1:1.

Experimental set-up and methodology

Coagulation-flocculation and adsorption experiments were conducted in a Phipps and Bird Jar-test apparatus (PB-600) using 1L leachate sample. Coagulation-flocculation pretreatment experiments started with rapid mixing for 2 min followed by slow mixing for 30 min. The pretreated or coagulated supernatant was further subjected to adsorption treatment by *Parkia Speciosa* pods activated carbon for 3 hours at 250 rpm. After 30 min settling time, the adsorbed supernatant was withdrawn from the beakers, filtered and used for further chemical analysis. All experiments were performed in triplicates and the results obtained were presented based on the average values.

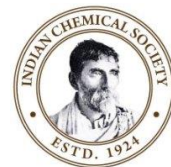
Leachate characterization

The leachate samples were analyzed for various Physico-chemical parameters such as pH, turbidity, electrical conductivity, alkalinity, total solids, total dissolved solids, total suspended solids, COD, BOD₅, chlorides, nitrate, calcium, fluoride and total iron as per Standard procedures¹⁹. pH and electrical conductivity were recorded at the sampling site with digital pH and electrical conductivity meter. All the characterization processes were carried out at an ambient temperature of 25 \pm 2°C, as Manipur State is situated in the north-eastern part of India where a tropical moderate climate prevails.

Results and discussions

Characterization of leachate

The characterization data of both fresh and stabilized leachate from the sanitary landfill site of Lamdeng Khunnou Solid Waste Management Plant are shown in Table 1. It can be observed from Table 1 that fresh leachate has a higher concentration of chemical parameters as compared to stabilized leachate except for pH and total suspended solids. The pH of fresh leachate was observed in the range of 6.8-



7.2, whereas the older stabilized leachate was found to be alkaline with pH ranging from 7.9-8.1. The lower pH of fresh leachate may be attributed to the high concentration of volatile fatty acids (VFAs)²². As fatty acids can be partially ionized during anaerobic decomposition, the concentration of free volatile acids decreased which contributed to higher pH of stabilized leachate²³. The higher total suspended solids concentration of stabilized leachate was due to the exposure of stabilized leachate stored in sump ponds which were exposed to the atmosphere. The relatively high values of electrical conductivity, 14.70 ms/cm and 6.55 ms/cm for fresh leachate and stabilized leachate respectively, indicated the presence of dissolved inorganic materials in the samples. Electrical Conductivity of raw leachate as high as 19.6 ms/cm, was reported²⁴. The presence of 6400 mg/L and 2880 mg/L COD for fresh and stabilized leachate respectively indicated high organic strength. However, comparatively lesser concentrations of 1280 mg/L and 420 mg/L BOD for fresh and stabilized leachate respectively show that majority of the compounds present in the leachate were non-biodegradable. This was due to the segregation of organic biodegradable waste for waste - to - compost treatments (70.6% of MSW collected) at the waste processing site, before the collected MSW were dumped in the landfill¹⁸. MSW composting diverts the biodegradable organic waste materials from entering the landfill, thus reducing the load on the landfill and consequently decreases the BOD₅ concentration of leachate. BOD₅/COD ratio shows the degree of biodegradation and gives information regarding the age of landfills. A slightly higher BOD₅/COD ratio of 0.2 for fresh leachate as compared to 0.14 for stabilized leachate, indicated a higher concentration of organic matter in fresh leachate. A lower BOD₅/COD ratio of 0.14 for stabilized leachate indicated that almost all organic matters had been decomposed anaerobically with time in stabilized leachate. The reason behind the BOD₅/COD ratio for the fresh leachate not greater than 0.2, might be because Landeng landfill has been in operation for four years only. The possible sources of 3422 mg/L and 2789 mg/L chloride concentration for fresh and stabilized leachate respectively are food wastes from kitchens and hotels. The presence of

41.76 mg/L and 25 mg/L total iron for fresh and stabilized leachate respectively, indicated the presence of steel and iron industrial waste reaching the landfill site. The brown colour of the leachate is mostly contributed by the oxidation of ferrous ions to ferric ions with the formation of ferric hydroxide colloids and complexes with fulvic/humic substance²⁵.

Pretreatment of leachate by coagulation-flocculation

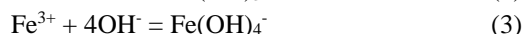
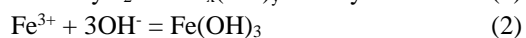
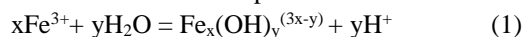
The pretreatment of leachate by coagulation-flocculation was carried out to minimize the high concentration of colloids that create turbidity in leachate. Even if the turbidity values of fresh and stabilized leachate were within the permissible limit prescribed by CPCB (Table1), the high concentration of colloids that create turbidity interfered with the adsorption process. These colloids are also organic in nature and they contribute to some parts of COD. The pretreatment by coagulation-flocculation not only removed turbidity that hinders the adsorption process but also resulted in partial removal of COD. Coagulation-flocculation experiments were carried out for both fresh and stabilized leachate by varying the pH of the leachate samples of 1L volume using the same dose of aluminium sulphate, ferric chloride and polyaluminium chloride to study the effect of pH on turbidity removal. After optimization of pH, varying doses of all the three coagulants were used with leachate samples of optimum pH to study the effect of coagulant dose on turbidity removal for both types of leachate.

Effect of pH on Turbidity removal by coagulation-flocculation

The effect of pH on turbidity removal was studied with prior adjustment of pH (4, 5, 6, 7, 8 and 9) for fresh leachate and pH (2, 4, 6, 8, 10 and 12) for stabilized leachate, using aluminium sulphate, ferric chloride and polyaluminium chloride. pH adjustment of fresh leachate was done using concentrated H₂SO₄ and NaOH solutions whereas 2N H₂SO₄ and 2N NaOH were used to adjust pH for stabilized leachate. For fresh leachates, the turbidity removal efficiencies were very low at pH<4 and and pH>9 and the values were discarded. Using the same coagulant dose of 8 g/L for fresh leachate and 4 g/L for stabilized leachate of all the three coagulants, the optimum working pH was



determined for fresh and stabilized leachate. The optimum pH of all the three coagulants was found to be 4 for both fresh and stabilized leachate. For fresh leachate, the maximum turbidity removals were observed to be 87.48%, 91.65%, 93.25% using aluminium sulphate, ferric chloride and polyaluminium chloride respectively at pH 4 (Fig.1). It can be seen from the graph that, after the optimum pH 4, the turbidity removal declined when the pH is increased, with the minimum turbidity removals of 26.28%, 60.68% and 66.22% at pH 8 for aluminium sulphate, ferric chloride and polyaluminium chloride respectively. The results obtained were in a similar trend²⁶ and it can be concluded that the acidic medium was better than the basic medium for the removal of impurities and pollutants from fresh leachate. For stabilized leachate, the maximum turbidity removals were observed to be 70.31%, 90.56%, 96.8% using aluminium sulphate, ferric chloride and polyaluminium chloride respectively at pH 4 (Fig.2). It can be seen from the graph that, after the optimum pH 4, the turbidity removal decreased with an increase in pH for all the three coagulants with the minimum turbidity removals of 6.71%, 72.39% and 80.81% at pH 8 for aluminium sulphate, ferric chloride and polyaluminium chloride respectively. The turbidity removal also decreased at pH 2 with turbidity removals of 29.06%, 78.43% and 92.24% for aluminium sulphate, ferric chloride and polyaluminium chloride respectively. The removal efficiencies were better in the acidic medium than in the basic medium and the various species of hydrolyzed ferric ions explains the phenomenon¹⁰. In the acidic medium, ferric ions can hydrolyze and form poly-nuclear cations as shown in Eq.(1). In the basic pH, these ferric ions react with hydroxyl (OH⁻) and form Fe(OH)₃ or Fe(OH)₄⁻ as shown in Eq.(2) and Eq.(3). As all colloidal impurities in water are negatively charged, polynuclear cations in the acidic pH are more preferable for the negative colloids than the anions in the basic pH¹².



In basic pH, polyaluminium chloride can be converted to Al(OH)₃ which remains in suspension

thus increasing turbidity. A similar trend of decreasing removal efficiencies of turbidity was observed with an increase in pH after pH 4 and it can be concluded that the acidic medium was better than the basic medium for impurities and pollutants removal from stabilized leachate (Fig.2).

Effect of coagulant dose on Turbidity removal by coagulation-flocculation

The optimum dosage of all the three coagulants was determined at a varying dosage of 5 g/L – 12 g/L at 1 g/L dose interval for fresh leachate and 1 g/L – 12 g/L at 1 g/L dose interval for stabilized leachate at the optimized pH 4. For fresh leachate, the optimum doses of aluminium sulphate, ferric chloride and polyaluminium chloride were observed as 8 g/L with corresponding turbidity removal of 88.68%, 91.2%, and 93.2% respectively (Fig.3). For stabilized leachate, the optimum doses of aluminium sulphate, ferric chloride and polyaluminium chloride were observed as 4 g/L, 3 g/L and 4 g/L respectively with the corresponding turbidity removals of 70.93%, 90.18% and 96.11% (Fig.4). It can be observed that further increase in coagulant dosages beyond the optimum doses, did not considerably increase the removal efficiencies of turbidity for both fresh and stabilized leachate (Fig.3 and Fig.4) and this follows the phenomenon of sweep flocculation and the theory of charge neutralization. When aluminium sulphate or ferric chloride or polyaluminium chloride was mixed with leachate, the hydrolyzed species of Al³⁺ or Fe³⁺ interacted with the negatively charged colloids and their charge get neutralized, making the colloids to destabilize. Beyond optimum dose, the colloids absorbed the cations after which they carry positive charge and become stable because of electrical repulsion¹⁰. As fresh leachate has a higher concentration of chemical parameters as compared to stabilized leachate, a comparatively higher dosage of coagulant is required for treating fresh leachate.

Effect of pH on COD removal by coagulation-flocculation

Apart from turbidity removal, some part of COD which were incorporated with the colloids and were in settleable form, also gets removed during the coagulation-flocculation process. Using 8 g/L aluminium sulphate, ferric chloride and



polyaluminium chloride at their optimized pH 4, the COD removals of 80%, 90% and 75% were observed respectively for fresh leachate (Table 2). For stabilized leachate, the COD removals were 55.55%, 77.78% and 77.78% using aluminium sulphate, ferric chloride and polyaluminium chloride respectively (Table 2). For fresh leachate, the COD removal rates ranged from 15% at pH 8 to 80% at pH 4 using aluminium sulphate, 60% at pH 9 to 90% at pH 4 using ferric chloride and 20% at pH 8 to 75% at pH 4 using polyaluminium chloride. The removal efficiencies of COD decreased after pH 4, with increasing pH till pH 8 (Table 2) and this is in accordance with the results²⁶ that aluminium sulphate can remove higher COD removal of 30% at pH 4 than 26.9% and 13% at pH 6 and 12 respectively. For stabilized leachate, the COD removal rates ranged from 11.11% at pH 8 and 12 to 55.55% at pH 4 using aluminium sulphate, 33.33% at pH 8 to 77.78% at pH 4 using ferric chloride (Table 2). It can also be observed that the removal efficiencies was better in the acidic medium than in the basic medium and the various species of hydrolyzed Al^{3+} and Fe^{3+} ions explains the phenomenon¹⁰. A removal of COD by 55.3% at acidic pH 5.2 and 3.1 g/L ferric chloride dose by coagulation-flocculation was reported²⁷. Using polyaluminium chloride, the removal rates of COD ranged from 44.44% at pH 12 to 77.78% at pH 4 (Table 2) and this is in accordance with the results²⁸ yielding in COD removal of 55% at an optimum 250 mg/L polyaluminium chloride at pH 6. For all the three coagulants, a similar trend of decreasing removal efficiencies of COD was observed with an increase in pH after pH 4 for both types of leachate (Table 2) and it can be concluded that the acidic medium was better than the basic medium for impurities and pollutants removal in leachate.

Effect of coagulant dose on COD removal by coagulation-flocculation

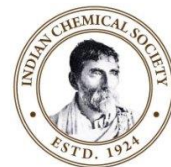
The optimum doses of aluminium sulphate, ferric chloride and polyaluminium chloride for fresh leachate were found to be 8 g/L with corresponding COD removals of 80%, 90% and 75% respectively at the optimized pH 4 (Table 3). For stabilized leachate, the optimum doses of aluminium sulphate, ferric chloride and polyaluminium chloride were found to be 4 g/L, 3 g/L and 4 g/L with the corresponding COD

removals of 55.55% using aluminium sulphate, 77.78% using ferric chloride and polyaluminium chloride (Table 3). 45% and 60% COD removals using aluminium sulphate and ferric chloride respectively at 2g/L optimum dose of both coagulants at pH 5 were reported²⁹. It can be observed that further increase in coagulant dosages beyond the optimum doses, did not considerably increase the removal efficiencies of COD also for both fresh and stabilized leachate (Table 3) and this follows the phenomenon of sweep flocculation and the theory of charge neutralization. To standardize the low-cost aluminium sulphate coagulant requirement, a linearised mathematical relation was developed between aluminium sulphate dose Vs reduction in turbidity and COD. The correlation coefficient (R^2) of 0.984 and 0.969 for fresh leachates (Fig.5) were observed for turbidity and COD against that of 0.955 and 0.941 for stabilized leachates (Fig.5). For validation of the equations, experimental and predicted values of turbidity and COD were tested with Chi-square (χ^2) (Eq.4) and observed lesser error for fresh leachate with turbidity and COD χ^2 values of 0.02 – 0.031 and 0.005 – 0.163 respectively against 0.074 – 1.872 and 0.001 – 0.978 respectively for stabilized leachates. These findings suggest better fit models on fresh leachate and thus can minimize the reactor requirement for leachate stabilization. Aluminium sulphate pretreated leachate was further used for the adsorption studies.

$$\chi^2 = \frac{(\text{Experimental} - \text{Predicted})^2}{\text{Experimental}} \quad (4)$$

Treatment of pretreated leachate by adsorption

As the aluminium sulphate pretreated effluent still had COD above the permissible limits or was not yet in sewage concentration levels, the pretreated effluent needs to be treated further by adsorption for the removal of the remaining COD in the pretreated leachate. The coagulated leachate (pretreated) was then subjected to adsorption by powdered activated carbon derived from *Parkia Speciosa* (Petai) pods. During the adsorption process, rapid COD adsorption was observed during the first 20 minutes followed by a slow diffusion adsorption process reaching adsorption equilibrium within 90 minutes for both fresh and stabilized leachate. For fresh leachate, 25% COD removal using 10 g/L



adsorbent dose and 47.5% COD removal using 20 g/L adsorbent dose were observed at an equilibrium time of 40 min and 20 min respectively (Fig.6) from an initial COD concentration of 1280 mg/L after pretreatment. Experimentally, the maximum adsorption from fresh leachate using 10 g/L and 20 g/L adsorbent dose were observed to be 32 mg/g and 30.4 mg/g at 40 min and 20 min equilibrium time respectively. For stabilized leachate, 81.25% COD removal using 5g/L adsorbent dose and 85% COD removal using 10g/L adsorbent dose were observed at an equilibrium time of 90 min and 20 min respectively (Fig.6) from an initial COD concentration of 1280 mg/L after pretreatment. Experimentally, the maximum adsorption from stabilized leachate using 5 g/L and 10 g/L adsorbent dose were observed to be 208 mg/g and 108.8 mg/g at 90 min and 20 min equilibrium time respectively. To check the adsorbent dose required for the reduction of COD of stabilized leachate below permissible limit of 100 mg/L, the adsorbent dose was increased to 20 g/L and observed an effluent of 96 mg/L suggesting effective adsorption by *Parkia Speciosa* (Petai) pods.

Diffusion kinetic model

To identify the mechanism of adsorption, the diffusion kinetic model was applied in the study. The initial rate of intraparticle diffusion was expressed by the following Eq.(5):

$$qt = k_p \cdot t^{1/2} \quad (5)$$

where, the rate constant of intraparticle diffusion (k_p) was obtained from the linear curve of the diffusion kinetic model of fresh and stabilized leachate (Fig.7). The graph of q_t Vs $t^{1/2}$ was plotted and shown in Fig.7. For validation of the equations, experimental and predicted values of qt (mg/g) were tested with Chi-square (χ^2) (Eq. 6) and are presented in Table 4. The correlation coefficient R^2 of 0.976 and 0.992 for fresh leachate and 0.964 and 0.992 for stabilized leachate were higher than 0.95 suggesting the fixing of data in the diffusion kinetic model. Further very lesser Chi-square (χ^2) values of 0.0130 and 0.0008 for fresh leachate and 0.0800 and 0.0009 for stabilized leachate for comparison of the experimental and predicted q_e confirms the application of this diffusion model of adsorption of COD on the Petai pod activated carbon. The diffusion coefficient k_p were 3.460 and 3.258 for

fresh leachate and 7.840 and 6.516 for stabilized leachate and the amount of COD adsorbed (q_e) were 32 mg/g and 30.4 mg/g using 10 g/L and 20g/L respectively for fresh leachate and 208.8 mg/g and 108.8 mg/g using 5 g/L and 10 g/L respectively for stabilized leachate.

$$\chi^2 = \frac{(\text{Experimental} - \text{Predicted})^2}{\text{Experimental}} \quad (6)$$

where, experimental value is the amount of COD adsorbed per gm of adsorbent obtained experimentally whereas predicted value is the predicted amount of COD adsorbed per gm of adsorbent.

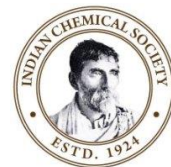
Conclusions

The coagulation-flocculation pre-treatment process of leachate led to very high removals of turbidity of 88.68%, 91.2% and 93.2% for fresh leachate using 8 g/L aluminium sulphate, ferric chloride and polyaluminium chloride respectively and corresponding removals from stabilized leachates was 55.55%, 77.78% and 77.78%. Though efficiency of aluminium sulphate was slightly lesser than ferric chloride and polyaluminium chloride, considering the less cost-effectiveness of aluminium sulphate and the nature of corrosive effluent using ferric chloride, aluminium sulphate was chosen as the optimal coagulant in this study. Further subjection of the pretreated effluent to adsorption by activated carbon derived from *Parkia Speciosa* (Petai) pods resulted in maximum COD removals of 47.5% and 85% from fresh and stabilized leachates respectively. Combining the pretreatment coagulation and adsorption, the overall COD removals were 89.5% and 93.33% from fresh and stabilized leachate respectively and the corresponding maximum adsorptions were 32 mg/g and 208 mg/g. COD of effluent below permissible limit of 100 mg/L was achieved by increasing the adsorbent dose to 20 g/L for stabilized leachate. Therefore the combined treatment process of coagulation-flocculation by aluminium sulphate and adsorption by activated carbon derived from *Parkia Speciosa* (Petai) pods proved to be an effective coupling method for leachate treatment.

Conflict of interest

The authors hereby declare that there is no conflict of interest for this manuscript.

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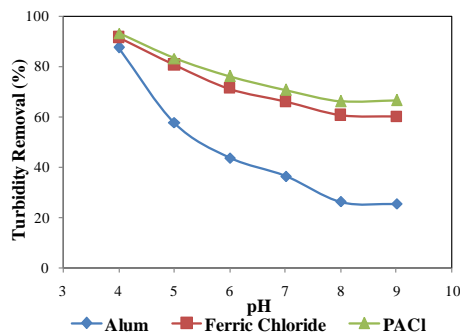


Fig. 1. Effect of pH on turbidity removal for fresh leachate.

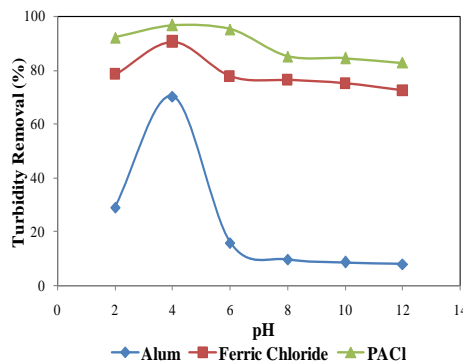




Fig. 2. Effect of pH on turbidity removal for stabilized leachate.

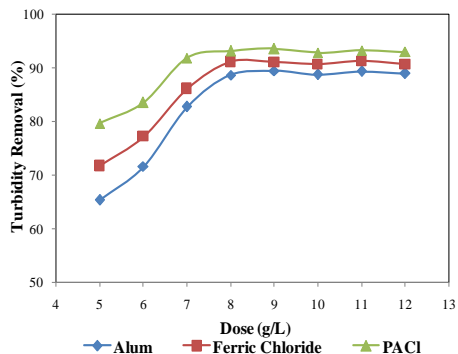


Fig. 3. Effect of coagulant dose on turbidity removal for fresh leachate.

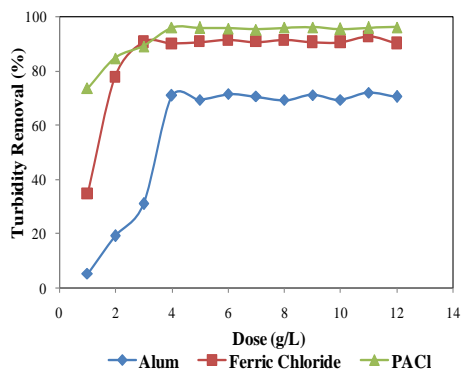


Fig. 4. Effect of coagulant dose on turbidity removal for stabilized leachate.

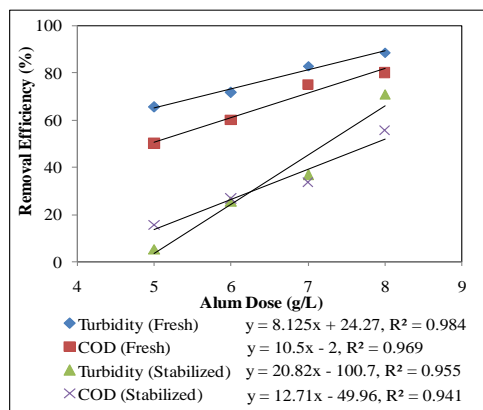


Table 1. Initial Physico-chemical characteristics of raw leachate from Lamdeng landfill.

Sl.	Parameters	Fresh leachate	Stabilized Leachate	Permissible Limit, CPCB-2017
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Fig. 5. Effect of aluminium sulphate dose on turbidity and COD removal for fresh and stabilized leachate.

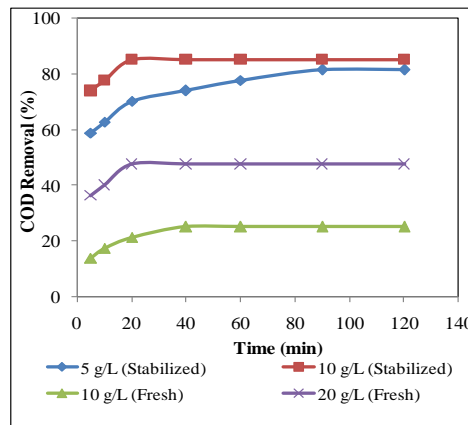


Fig. 6. Effect of adsorption time on COD removal.

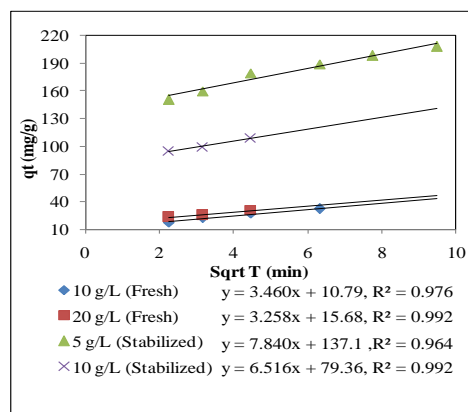
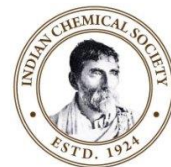


Fig. 7. Diffusion kinetic model for fresh and stabilized leachate.



1	pH	7.15	8.01	5.5 – 9
2	Conductivity, ms/cm	14.70	6.55	-
3	Turbidity, NTU	175	161	300
4	Chloride, mg/L	3422	2789	500
5	Total Solids, mg/L	10889	5668	-
6	Total Dissolved Solid, mg/L	9849	4388	1200
7	Total Suspended Solid, mg/L	1040	1280	600
8	COD, mg/L	6400	2880	100
9	BOD ₅ , mg/L	1280	420	50
10	BOD ₅ /COD	0.2	0.14	-
11	Total Alkalinity, mg/L	3700	2520	-
12	Nitrate, mg/L	320	184	20
13	Fluoride, mg/L	0.68	0.59	15
14	Calcium, mg/L	524	398	100
15	Total iron, mg/L	41.76	25	3

Table 2. Effect of pH on COD removal by coagulation-flocculation.

Fresh Leachate				Stabilized Leachate			
pH	Aluminium sulphate	Ferric Chloride	Polyaluminium chloride	pH	Aluminium sulphate	Ferric Chloride	Polyaluminium chloride
4	80.00	90.00	75.00	2	33.33	44.44	55.55
5	70.00	85.00	70.00	4	55.55	77.78	77.78
6	43.75	70.00	50.00	6	22.22	66.67	77.78
7	25.00	60.00	40.00	8	11.11	33.33	55.55
8	15.00	65.00	20.00	10	22.22	55.55	55.55
9	20.00	60.00	30.00	12	11.11	44.44	44.44

Table 3. Effect of coagulant dose on COD removal.

Fresh Leachate				Stabilized Leachate			
Dose (g/L)	Aluminium sulphate	Ferric Chloride	Polyaluminium chloride	Dose (g/L)	Aluminium sulphate	Ferric Chloride	Polyaluminium chloride
5	50.00	60.00	40.00	1	15.42	25.83	33.33
6	60.00	70.00	50.00	2	26.53	55.55	44.44
7	75.00	85.00	70.00	3	33.33	77.78	55.55
8	80.00	90.00	75.00	4	55.55	77.78	77.78

Table 4. Adsorption details of fresh and stabilized leachate.

Fresh Leachate					Stabilized Leachate				
Adsorbent dose (g/L)	q _e (mg/g)	R ²	kp	χ ²	Adsorbent dose (g/L)	q _e (mg/g)	R ²	kp	χ ²
10 g/L	32.0	0.976	3.460	0.0130	5 g/L	208.8	0.964	7.840	0.0800
20 g/L	30.4	0.992	3.258	0.0008	10 g/L	108.8	0.992	6.516	0.0009