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Adsorption study on municipal solid waste leachate using *Moringa oleifera* seed

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Abstract Effects of initial concentrations of Moringa oleifera seed coagulant for removing Chemical Oxygen Demand and Total Dissolved Solids from municipal solid waste leachate have been evaluated at an optimum pH of 7 and temperature of 318 K. The kinetic data obtained from the experiments were fitted to the pseudo first-order, pseudo second-order, Elovich and intraparticle diffusion models. Based on a regression coefficient (R^2) , the equilibrium (kinetic) data were best fitted with the Elovich model $(R^2 = 0.993$ for Chemical Oxygen Demand and $R^2 = 0.996$ for Total Dissolved Solids) than that of other models. The results of the kinetic models study indicated that the adsorption capacity of M. oleifera seed as a coagulant for removing Chemical Oxygen Demand and Total Dissolved Solids in a leachate increased up to 100 mg L^{-1} , beyond which the adsorption capacity got reduced. Finally, the present study concluded that *M. oleifera* seed coagulant could be employed effectively for the removal of Chemical Oxygen Demand and Total Dissolved Solids in a municipal solid waste leachate.

Keywords Chemical Oxygen Demand · Kinetic models · Regression analysis · Total Dissolved Solids

Introduction

Municipal solid wastes (MSWs) are unavoidable products, disposed by various human activities. The solid wastes are

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Vel Tech High Tech Dr. Rangarajan Dr. Sakunthala Engineering College, Affiliated to Anna University Chennai, No. 60, Avadi-Vel Tech Road, Avadi, Chennai 600 062, Tamil Nadu, India e-mail: sivakumar.ijest@gmail.com categorized primarily based on the place of generation viz., urban, rural and industrial areas (Tchobanoglous et al. 1993a). Proper disposals of these solid wastes are imperative. The most common method of disposal of solid wastes is by land filling (Mishra and Mani 1993; Tchobanoglous et al. 1993a, b). The composition of MSWs depends on industrialization, urbanization, waste management and local conditions. Incorrectly secured and improperly operated MSWs landfills pose a serious threat to the environment, mainly to the surface water and groundwater (Demetracopoulos et al. 1984; Karfiatis and Demetracopoulos 1984). The scale of this threat depends on the quantity, quality and composition of the leachate and the distance of a landfill from water sources (Słomczyńska and Słomczyński 2004). MSW leachate is considered as highly concentrated complex effluent, which may contain dissolved mineral and organic compounds (humic substances, fatty acids and aromatic compounds), inorganic macro components, heavy metals, xenobiotic organic compounds and many other hazardous chemicals (Peter et al. 2002; Tchobanoglous et al. 1993a, b). The generated amount of leachate depends on initial water content of MSWs and on the storage or disposal conditions such as temperature, humidity and ventilation (Sivakumar and Pushpakaran 2010a, b).

Thus, knowledge of the quantity, quality and composition of leachate is necessary when designing the treatment facilities and it is important in determining raw leachate pollution effect on the environment (Słomczyńska and Słomczyński 2004). Due to simplicity and cost-effectiveness, the adsorption method has been widely used (Babel and Kurniawan 2003; Ho and McKay 1998) to control the various pollutants from the water and wastewater. Exploration of good low-cost and non-conventional adsorbents may contribute to the sustainability of the environment and



offer promising benefits for the commercial purpose in a future. The costs of the activated carbon prepared from biomaterials are negligible when compared with the cost of commercial activated carbon. Some of the activated carbons (prepared from agro-based wastes) used to treat the industrial wastewater in the recent past are corncob, groundnut husk, rice husk, tea leaves carbon, saw dust (Nigam and Rama 2002) eucalyptus bark (Aravind and Prem 2003) and agricultural wastes (Adinata et al. 2007).

The use of natural materials of plant origin to purify water and wastewater is not a new idea. This study mainly pays attention to Moringa oleifera, a natural material of plant origin, used to purify municipal solid waste leachate. M. oleifera belongs to the family Moringaceae. M. oleifera originates in India and spread throughout the tropics from Northeastern Pakistan (from 33°N to 73°E) to Northern West Bengal State in India and Northeastern Bangladesh. It can grow at elevations from sea level to 1,400 m (Ramachandran et al. 1980). It is cultivated in most parts of Pakistan, India, and Nepal, as well as in Afghanistan, Bangladesh Sri Lanka, Southeast Asia, West Asia, the Arabian Peninsula, East and West Africa, throughout the West Indies and Southern Florida, in Central and South America from Mexico to Peru, as well as in Brazil and Paraguay (Jahn et al. 1986). M. oleifera is a slender softwood tree that branches freely and can grow extremely fast to a height of 10 m. It will survive in a temperature range from 25 to 40 °C, but has been known to tolerate temperature of 48 °C and light frosts. M. oleifera grows neutral to slightly acidic soils and grows best in well-drained loam to clay-loam. It tolerates clay soils but does not grow well in waterlogged condition.

Among other plant materials, powder form of M. oleifera seed has been proven to be one of the most effective and viable replacements of various chemical coagulants (Nwaiwu and Lingmu 2011; Sanchez-Martin et al. 2010; Amagloh and Benang 2009; Ndabigengesere and Narasiah 1998a; Jahn 1988) for treating water (Muyibi et al. 2001; Muyibi and Evison 1995a, b) and wastewater (Daniyan et al. 2011; Muyibi et al. 2002; Ndabigengesere and Narasiah 1998b; Ndabigengesere et al. 1995; Olsen 1987). Further, the powder form of M. oleifera is used to remove the heavy metals and surfactants (Beltrán- Heredia and Sánchez-Martín 2008, 2009) from water and wastewater. The use of *M. oleifera* seed powder has an added advantage over the chemical treatment of water and wastewater, as it is biological and edible. The powder joins with the materials and contaminants in the aqueous solutions and sinks to the bottom (Varsha and Punita 2010) of any treatment units. This treatment also removes 90-99 % of bacteria



contained in water (Katayon et al. 2005). High-quality activated carbon prepared from the waste husks of *M. oleifera* (Miquel and Wendy 2010; Pollard et al. 1995) is used to purify the water and *M. oleifera* pods are efficient in absorbing organic pollutants and pesticides (Akhtar et al. 2007a, b). In addition, dehusked *M. oleifera* press cake is efficient in the removal of hydrophobic organic pollutants from water (Boucher et al. 2007) and the extracted part of *M. oleifera* seeds prevents the growth of coliforms, sodomonas and aeroginosen and as a result, reduces the requirement for disinfection (Yarahmadi et al. 2009; Caceres 1991).

Thus, the aim of present study was to investigate the effect of initial concentration of *M. oleifera* seed coagulant for removing Chemical Oxygen Demand (COD) and Total Dissolved Solids (TDS) in a municipal solid waste leachate. Further, the experimental data were fitted to various kinetic models like pseudo first-order, pseudo second-order, Elovich and intraparticle diffusion models for determining the suitability of *M. oleifera* seed as a coagulant in removing COD and TDS from a municipal solid waste leachate. All experiments were conducted in the Environmental Engineering Laboratory, Department of Civil Engineering, Easwari Engineering College, Tamil Nadu, India, during December 2010.

Materials and methods

Moringa oleifera seeds were purchased from the local market, Thanjavur, Tamil Nadu, India. The chemical properties of M. oleifera seed are listed in Table 1. The seeds were dried and dehusked mechanically by removing the seed wings and coat. The white seed kernels were pulverized and sieved through a 0.75-mm sieve. 100 mg of powdered form of M. oleifera seed was mixed with 11 of distilled water, stirred with a stirrer for a period of 30 min and finally the stirred solution kept for a period of 24 h to generate a coagulant. After a period of 24 h, the required amount of coagulant was taken for conducting the experiments, and the remaining quantity was kept in the refrigerator at a temperature of 278 K. This method was used to avoid the decomposition of coagulant, because the M. oleifera seed coagulant is an agro-based product. Recent study has also proven that extracted form of active coagulant from the M. oleifera seeds are unstable and normally deteriorate when stored under room conditions and cause decrease in its coagulation property (Saulawa et al. 2011).

The total nine solid waste samples of 1 kg each were collected from a center (three samples), boundary (three samples) and between center and boundary (three samples) of Thanjavur Municipality Dumping Yard, Tamil Nadu,

Table 1	The	chemical	properties	of M	loringa	oleifera	seed
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S. No.	Properties of Moringa oleifera seed	Values
1	Proximate properties	
	Moisture (%)	71.3
	Ash (%)	2.3
	Carbohydrate (%)	3.7
	Fiber (%)	6.7
	Protein (%)	12.8
	Fat (%)	3.2
2	Mineral properties	
	Calcium (mg)	43.5
	Magnesium (mg)	13.6
	Potasium (mg)	186.2
	Phosporous (mg)	138.5
	Iron (mg)	16.5
	Sulfate (mg)	98.2

India. The age of the solid waste was known to be 6 months (data provided by the authority of Thanjavur Municipality). The average compositions of three samples (replicates) collected from each center, boundary, between a center and boundary, respectively, were determined and are presented in Table 2. Further, overall average compositions of solid waste at Thanjavur Municipality Dumping Yard were determined, and the compositions are presented (Table 2) in percentage. (i.e., reported as a weight basisratio of weight of each component in the sample to the total weight of the sample).

The solid waste collected from entire Thanjavur District was dumped into the Thanjavur Municipality Dumping Yard (landfill). The solid waste in a landfill was compacted by roller and the mass density of compacted solid waste was found to be 2,560 kg/m³ (the mass density of solid waste was calculated based on standard procedure stipulated by Gopal and Rao 2009). There was no natural drainage occurred at the landfill site, results, unable to collect a leachate from landfill directly. Thus, it is necessary to generate a leachate in the laboratory for further study. Before applying the distilled water over solid waste to obtain a leachate, solid waste collected from Thanjavur Municipality Dumping Yard was compacted into the container of size $0.3 \times 0.3 \times 0.5$ m $(\text{length} \times \text{breadth} \times \text{height})$ by compacting device. In order to simulate the field condition, a mass density of solid waste in the container was maintained at 2,560 kg m⁻³. After compaction, distilled water was applied over the solid waste directly to obtain an experimental fluid (leachate), and its quality was analyzed using a standard procedure (APPA, AWWA and WEF 2005). The present study mainly focused on reducing the COD and TDS concentrations in a leachate using M. oleifera seed as a coagulant at various initial concentrations. Since the age of solid waste is 6 months, the initial concentration of COD and TDS in an experimental leachate was found only to be 12,435 and 5.485 mg L^{-1} , respectively.

The previous studies discovered that the laboratory test results on untreated grab leachate samples showed high concentration of TDS (734 mg L^{-1}) and COD $(1,631 \text{ mg L}^{-1})$ (Azim et al. 2011). The COD concentration in a landfill leachate varied from 110 to 300 mg L^{-1} (Noor et al. 2011). TDS and COD concentration in a landfill leachate of Benin-City, Edo State, Nigeria was found to be $32,192 \pm 563.78$ and $91.47 \pm 1,30$ mg L⁻¹,

Table 2 Compositions of solid waste from Thanjayur	Components*	Places			
Municipality Dumping Yard		Center** (%)	Boundary** (%)	Between center and boundary** (%)	Average*** (%)
	Polythene milk sachets	11.4	10.9	10.8	11.4
	Vegetable food wastes (organic)	56.8	54.5	56.1	55.8
	Paper (news paper, card boards, etc.)	11.7	12.7	12.2	12.2
	Wood chips (plant, carpentry)	7.4	8.7	8.8	8.3
	Plastics (sheets, solid, bags, etc.)	3.8	4.3	4.2	4.1
* Components were identified by manually (eye validation)	Glass	1.9	1.6	1.6	1.7
	Cotton wastes (thread, cloth, sanitary napkins, etc.)	1.4	1.8	1.3	1.5
of three samples collected from each place	Metals (workshop waste, stainless steel, pins, etc.)	1.5	1.6	1.2	1.3
*** Overall average	Leather and rubber	1.2	1.3	1.4	1.2
composition of solid waste from	Others such as battery	2.9	2.6	2.4	2.5
Thanjavur Municipality Dumping Yard	Total	100.0	100.0	100.0	100.0



respectively (Aiyesanmi and Imoisi 2011). Amir and Ali 2011 studied about the characteristics of solid waste landfill leachate for four different landfills. The results showed that TDS and COD concentration varied from 1,123 to 17,500 mg L⁻¹ and from 250 to 4,852 mg L⁻¹, respectively at Shahrood's landfill. Further, TDS and COD concentration in Turkey's landfill varied from 209 to 4,418 mg L⁻¹ and 250 to 4,852 mg L⁻¹ respectively (Amir and Ali 2011). The change in temperature, climatic condition, soil used for land filling, organic and inorganic materials in the solid waste, age of the solid waste, other characteristics of solid waste and method of land filling are the main factors for changing the COD and TDS concentration in different landfills.

Leachate was filled in six glass beakers of one-liter capacity and placed in the Phipps and Bird jar test apparatus, which was used for evaluating and optimizing the coagulation process by M. oleifera seed coagulant. Adsorption of COD and TDS by M. oleifera seed coagulant was influenced by pH, temperature (Oluduro and Aderiye 2007; Katayon et al. 2004) and storage conditions (Katayon 2004, 2006a, b). To evaluate and optimize the coagulation process, experiments were conducted at different pH (4, 5, 6, 7, 8 and 9), different temperature (300, 306, 312, 318, 324 and 330 K) and different concentration (75 and 100 mg L^{-1}) with rapid mixing rotational speed of 100 rpm, slow mixing rotational speed of 20 rpm and settlement period of 60 min. The recommended settling time is 1 to 2 h for all the particles and contaminants to settle at the bottom of the storage container using M. oleifera seed (Nwaiwu and Lingmu 2011). Thus, after a settlement period of 60 min (in this study), the concentration of COD and TDS in a supernatant leachate was analyzed as per standard procedure given by APPA, AWWA and WEF (2005).

Further, the effects of M. oleifera seed coagulant for reducing COD and TDS in a solid waste leachate, batch adsorption tests were carried out in 100 mL flasks, immersed in a thermostatic shake water bath (to maintain the temperature). The agitation speed for the flasks was keeping at a constant speed of 100 rpm. The flasks wew shaken for the adsorption periods varying from 20 to 160 min. Batch experiments were carried out at different initial concentrations 20, 40, 60, 80, 100 and 120 mg L^{-1} at neutral pH (obtained from Figs. 1, 2) and at a temperature of 318 K (obtained from Figs. 3, 4). After various adsorption periods (20, 40, 60, 80, 100, 120, 140 and 160 min), the supernatant leachate in flasks was centrifuged at 2,500 rpm for 15 min. The concentration of COD and TDS in a supernatant leachate was analyzed as per the standard prescribed by APPA, AWWA and WEF (2005).

Using a mass balance, the concentration of COD and TDS at different adsorption periods by *M. oleifera* seed coagulant were calculated as

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{1}$$

in which, q_t is the amount of COD and TDS adsorbed by the *M. oleifera* seed coagulant at time 't', C_0 is the initial concentration of COD and TDS, C_t is the aqueous phase concentration of COD and TDS at time 't', 'V' is the volume of the aqueous phase and '*M*' is the weight of *M. oleifera* seed powder.

Many kinetic models propose to elucidate the mechanism of solute adsorption and potential rate controlling step. These include pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion equations (Parimalam et al. 2011; Igwe and Abia 2006; Ho and McKay 1998). The rate and mechanism of adsorption were controlled by various factors like physical and/or chemical properties of adsorbents, ambient temperature and solution pH (Oluduro and Aderiye 2007; Katayon et al. 2004). These four kinetic models are useful for the design and optimization of effluent-treatment process. Hence, the experimental data obtained from batch studies were fitted to the above four kinetic models for determining the suitability of *M. oleifera* seed coagulant for removing COD and TDS in a leachate.

The pseudo-first order equation of Lagergren is generally expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$
(2)

in which, q_e is the sorption capacity at equilibrium (mg/g), q_t is the sorption capacity at time 't' (mg/g), k_1 is the first-order rate constant (min⁻¹) and 't' is time (min). Hence, a linear trace is expected between the two parameters, $\log(q_e - q_t)$ and 't', provided the adsorption follows first order kinetics. The values of k_1 and q_e can be determined from the slope and intercept.

The pseudo-second order kinetic rate equation is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(3)

in which, K_2 is the second-order rate constant (mg g⁻¹ min⁻¹). A plot of t/q_t and 't' should give a linear relationship if the adsorption follows second order. q_e and k_2 can be calculated from the slope and intercept of the plot.

The Elovich equation is expressed as

$$q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{\ln(t)}{\beta} \tag{4}$$



in which, ' α ' is the initial sorption rate and ' β ' is the desorption constant. A plot of q_t versus $\ln(t)$ should give a linear relationship if the Elovich equation is applicable with a slope of $(1/\beta)$ and an intercept of $(\ln(\alpha\beta)/\beta)$.

The intraparticle diffusion equation is expressed as

$$q_t = k_p t^{1/2} + C \tag{5}$$

in which, k_{p} is the intraparticle diffusion constant.

Results and discussion

Effects of pH on COD and TDS removal

The pH is an important parameter for determining the adsorption capacity because it affects the solubility and degree of ionization of the adsorbate (Adelaja et al. 2011). Experiments were carried out at different initial pH (pH ranges from 4 to 9 with an increment of 1) to investigate the effects of initial pH on COD and TDS removal in a solid waste leachate at a concentration of 75 mg L⁻¹ (Fig. 1) and 100 mg L⁻¹ (Fig. 2), respectively. From Figs. 1 and 2, it may be observed that till pH value reaches 7, the removal percentage of COD and TDS increased, beyond which removal percentage got decreased. However, a significant change in percentage removal has observed between the pH value 6 and 8.

At low pH, hydrogen ions in the mixture were not allowing the ions to adhere with the binding sites of adsorbents. At high pH, a leachate becomes basic and amino acids present in the protein of *M. oleifera* would accept a proton from a leachate and released more hydroxyl groups making the solution more basic (Daniyan et al. 2011; Amagloh and Benang 2009); as a result, ions were



Fig. 1 Effects of pH on COD and TDS removal at a concentration of 75 mg L^{-1}



Fig. 2 Effect of pH on COD and TDS removal at a concentration of 100 mg L^{-1}

not adhering into the binding sites of adsorbents. However, between the pH value 6 and 8, more ions were adhering to the binding sites of adsorbents because of neutral nature of leachate. Thus, an optimum pH value leading to maximum COD and TDS removal percentage was found to be 7 (Figs. 1, 2). From Figs. 1 and 2, it was found that COD and TDS removal percentage by *M. Oleifera* seed coagulant at an optimum pH of 7 was 84.5 and 82.5 %, respectively, for a concentration of 100 mg L⁻¹ and 68.5 and 63.5 %, respectively, for a concentration of 75 mg L⁻¹.

Effects of temperature on COD and TDS removal

To investigate the effects of temperature on COD and TDS removal using M. oleifera seed coagulant, treatment was done at different temperatures viz., 300, 306, 312, 318, 324 and 330 K for a concentration of 75 mg L^{-1} (Fig. 3) and 100 mg L^{-1} (Fig. 4), respectively. As similar to pH, from 300 to 318 K temperature, the diffusion rates of the adsorbate molecules across the external boundary layer are high, yielding more adsorptions of COD and TDS by M. Oleifera seed coagulant (Figs. 3, 4). Beyond 318 K temperature, less adsorption was observed, because of low diffusion rate of the adsorbate molecules. Furthermore, at low and high temperatures, liberalization of a hydroxyl group from the amino acids presented in the protein of M. oleifera was low (leachate is more acidic condition) and high (leachate is basic condition), respectively. However, at 318 K, liberalization of a hydroxyl group from the amino acids present in the protein of M. oleifera was moderate, which is sufficient to create favorable environment for the ions to adhere to the binding sites of the adsorbents (Daniyan et al. 2011; Amagloh and Benang 2009). Thus, an optimum





Fig. 3 Effects of temperature on COD and TDS removal at a concentration of 75 mg L^{-1}



Fig. 4 Effects of temperature on COD and TDS removal at a concentration of 100 mg L^{-1}

temperature leading to maximum COD and TDS removal percentage was found to be 318 K (Figs. 3, 4). From Figs. 3, 4, it was found that COD and TDS removal percentage by *M. Oleifera* seed coagulant at an optimum temperature of 318 K was 83.3 and 81.5 %, respectively, for a concentration of 100 mg L⁻¹ and 72.2 and 68.5 %, respectively, for a concentration of 75 mg L⁻¹.

In order to validate the effects of pH and temperature on COD and TDS removal in a leachate, experiments have been performed with an optimum pH value of 7 (Figs. 1, 2) and temperature of 318 K (Figs. 3, 4). The results obtained at an optimum pH (7) and temperature (318 K) showed that maximum COD and TDS removal percentage by *M. Oleifera* seed coagulant was 84.5 and 82.6 %, respectively, for a concentration of 100 mg L⁻¹ and 75.1 and 70.9 %, respectively, for a concentration of 75 mg L⁻¹. Hence, kinetic model's study was performed by changing the

initial coagulant concentrations at an optimum pH (7) and temperature (318 K).

Adsorption kinetics

A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process (Maximova and Koumanova 2008). The experimental results of adsorption of COD and TDS by *M. oleifera* seed coagulant at various initial concentrations are shown in Figs. 5 and 6, respectively.

From Fig. 5, it can be observed that adsorption of COD by *M. oleifera* seed coagulant occurred very rapidly within the first 20 min and equilibrium occurred after 120 min. The same result was also observed for the adsorption of TDS by *M. oleifera* seed coagulant (Fig. 6). Further, with increased initial concentrations of coagulant from 20 to 120 mg L⁻¹, the adsorption of COD and TDS with *M. oleifera* coagulant increased. However, higher adsorption capacity of COD and TDS with *M. oleifera* coagulant obtained at 100 mg L⁻¹, because of *M. oleifera* seed



Fig. 5 Effects of *Moringa oleifera* seed coagulant for removing COD at various initial concentrations



Fig. 6 Effects of *Moringa oleifera* seed coagulant for removing TDS at various initial concentrations





coagulant has more active sites at 100 mg L^{-1} , beyond which the adsorption capacity got reduced (Figs. 5, 6). It may also be found from the aforementioned results that at 120 mg L^{-1} initial concentration, the *M. oleifera* seed coagulant has more active sites as similar to 100 mg L^{-1} initial concentrations. However, 120 mg L^{-1} initial concentration is not sufficient for adsorbing COD and TDS in a leachate, because, a coagulant itself produces more sludge. Thus, an optimum dosage for which the maximum removal of COD and TDS occurred at an initial concentration of 100 mg L^{-1} (Figs. 5, 6). At a concentration of 100 mg L^{-1} positively charged water-soluble proteins in a powder form of a M. oleifera seed kernel act like magnets and attract the predominantly negatively charged particles in an aqueous solution to form settleable flocs, leading to maximum removal by M. oleifera (Matthew et al. 2011).

In order to investigate the consistency, experimental data were fitted with the four kinetic model (pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion) equations. The plots of the four kinetic equations for removing COD and TDS from municipal solid waste leachate using M. *oleifera* seed as a coagulant at various initial concentrations are shown in Figs. 7 and 8, respectively. In order to measure the degree of relationship between two or more variables, the correlation and regression analysis were performed for all parameters.

From Fig. 7a, it may be found that the pseudo first-order rate constant k_1 for COD ranges between 0.014 and 0.065 min⁻¹. The correlation coefficient R^2 found to range from 0.918 to 0.946. It was found that the values for rate constant (k_2) of pseudo-second order kinetic model for COD decreases from 0.00138 to 0.00161 kg mg⁻¹ min⁻¹ (Fig. 7b) and the ' β ' value for COD varies between 0.0000324 and 0.0000575 with an increase of the initial concentrations from 20 to 120 mg L⁻¹ (Fig. 7c). The correlation coefficient R^2 for pseudo-second order model varies from 0.938 to 0.963 and correlation coefficient R^2 for Elovich kinetic model showed that very high







correlation was developed between two variables and that the values vary from 0.952 to 0.993. Further, a value of k_p for the interapartical kinetic model for COD varies from 4,290.6 to 8,782.6 and R^2 value varies from 0.923 to 0.965 (Fig. 7d).

From Fig. 8a, it may be found that the pseudo first-order rate constant k_1 for TDS ranges between 0.009 and 0.013 min⁻¹. The correlation coefficient R^2 was found to range from 0.929 to 0.949. It was found that the values for rate constant (k_2) of pseudo-second order kinetic model for TDS decreases from 0.0023 to 0.0051 kg mg⁻¹min⁻¹ (Fig. 8b) and the ' β ' value for TDS varies between 0.000076 and 0.000141 with an increase of the initial concentrations from 20 to 120 mg L⁻¹ (Fig. 8c). The correlation coefficient R^2 for pseudo-second order model varies from 0.931 to 0.978 and correlation coefficient R^2 for Elovich kinetic model showed that very high correlation was developed between two variables, and the values vary from 0.963 to 0.996. Further, a value of k_p for the interapartical kinetic model for TDS varies from 1,759.3 to 3,363.5 and R^2 value varies from 0.959 to 0.977 (Fig. 8d).

The summary of regression equations and R^2 for COD and TDS removal obtained at an initial concentration of 100 mg L⁻¹ (higher adsorption capacity of COD and TDS in a municipal solid waste leachate has found at an initial concentration of 100 mgL⁻¹) are given in Table 3. From Table 3, it may be found that equilibrium (kinetic) data found fitted well with Elovich kinetic model ($R^2 = 0.993$ for COD and $R^2 = 0.996$ for TDS) than that of other models.

Results from Figs. 7 and 8 and from Table 3 indicate that equilibrium COD and TDS data fitted well with Elovich kinetic model than that of other models. Thus, the study informed that Elovich kinetic model was used to elucidate the mechanism of COD and TDS adsorption in a municipal solid waste leachate using *M. oleifera* seed as a coagulant and is useful for design and optimization of COD and TDS removal treatment processes.

Models	Parameters						
	COD	TDS					
	Regression equation	R^2	Regression equation	R^2			
Pseudo first-order kinetic model	$Y = 0.0108994 \ X + 3.1457$	0.946	$Y = 0.00976268 \ X + 2.9732$	0.949			
Pseudo-second order kinetic model	$Y = 1.24548 \times 10^{-5} X + 0.0014$	0.963	$Y = 3.00673 \times 10^{-5} X + 0.0035$	0.978			
Elovich kinetic model	$Y = 1,7384.5 \ X - 41,540.70$	0.993	Y = 7,093.34 X - 17,092.10	0.996			
Interapartical kinetic model	$Y = 4,290 \ X - 5,521.74$	0.965	$Y = 1,759.04 \ X - 2,473.81$	0.977			

Table 3 The regression equations and R^2 for COD and TDS removal obtained at an initial concentration of 100 mg L⁻¹

The adsorption capacity of M. oleifera of this study has been verified with the adsorption capacity of M. oleifera of previous investigators. Asrafuzzaman et al. (2011) found that the maximum reduction of total coliform counts (cfu/100 mL) and turbidity using 100 mg L^{-1} M. oleifera was 96.00 and 94.10 %, respectively. After 24 h of settling time, maximum removal efficiency achieved by M. oleifera seed coagulant was 96.34 % for turbidity, 88.89 % for color and 26.50 % for total suspended solids in an aqueous solution (Nwaiwu and Lingmu 2011). Nwaiwu and Lingmu 2011 achieved 94.56 % of microbial population removal. Sarah and Susan 2011 achieved 90.00 % of bacterial removal using M. oleifera coagulant in an aqueous solution. The results of Katayon et al. (2004, 2005, 2006a) and Muyibi and Evison (1995b) indicated that M. oleifera seed extract may not be an efficient coagulant for low turbid water. However, the extract of M. oleifera seed was used to reduce the hardness to 70.00 % as well as turbidity to 99.00 % in hard water (Muyibi and Evison 1995a). Furthermore, the extract efficiency of M. oleifera seed for turbidity removal equals that of alum according to the study conducted by Muyibi and Alfugara (2003). The same observations were also made by Yarahmadi et al. (2009). The concentration reduction obtained for a concentration of 10 g L^{-1} of *M. Oleifera* seed kernels powder has similar effect as that of conventional coagulum and alum (Amagloh and Benang 2009). The maximum removal percentage of lead in an aqueous solution was found to be 48.40 % with 180 min contact time using ground *M. oleifera* pods (Adelaja et al. 2011) and 97.00 % of the algae present in the raw Nile water were removed (Shehata et al. 2002) using M. oleifera coagulant.

Salwa et al. (2011) conducted the experiments to remove color from a landfill leachate. Without addition of ZnO, color removal of 88.80 % was achieved at the pH of

5 and at a contact time of 90 min, and with the addition of 0.2 g of ZnO gave the highest color removal of 90.10 % at 60 min from a landfill leachate (Salwa et al. 2011). Corneliu et al. (2010) has studied the sorption of Cu in a leachate using moss peat as biosorbent. The results indicated that a removal rate of Cu was 95.00 % (Corneliu et al. 2010). The adsorption of Cu, Zn and Fe reached the maximum removal condition after 5 h with a removal efficiency of 41.29, 58.94 and 52.03 %, respectively, by dead fungal biomass from a landfill leachate (Abdullah et al. 2011).

In general, the costs of activated carbon prepared from biomaterials are negligible when compared with the cost of commercial activated carbon (Nigam and Rama 2002). Further, the cost of this natural coagulant would be less expensive compared with the conventional coagulant (alum) for water and wastewater purification (Okuda et al. 1999, 2001; Broin et al. 2002) since it is available in most rural communities (Gideon and Richardson 2010). Because of the abundance source, low price, multi-purposes, biodegradation properties (Yarahmadi et al. 2009; Sharma et al. 2006; Katayon et al. 2005), better coagulation properties (Nwaiwu and Bello 2011) and antimicrobial properties (Amagloh and Benang 2009), M. oleifera can be encouraged to use in water and wastewater purification purposes. Definitely, this coagulant process using *M. oleifera* is likely to reduce the high cost of the current water and wastewater treatment systems.

Conclusion

Adsorption of COD and TDS by *M. oleifera* seed coagulant was influenced by pH and temperature. The maximum removal of COD and TDS in a leachate occurred at an



optimum pH of 7 and an optimum temperature of 318 K. In order to validate the effects of pH and temperature on COD and TDS removal in a leachate; experiments have been performed by changing the initial coagulant concentration, by keeping constant optimum pH (7) and by keeping constant optimum temperature (318 K). The experimental data were also fitted to various kinetic models viz., pseudo first-order, pseudo second-order, Elovich and intraparticle diffusion models. The results of the present study indicated that the adsorption capacity of M. oleifera coagulant for removing COD and TDS in the municipal solid waste leachate increased with increasing of initial concentration $(20-120 \text{ mg L}^{-1})$. It could be found that adsorption of COD and TDS by M. oleifera coagulant occurred very rapidly within the first 20 min and equilibrium occurred at 120 min. Further, the maximum adsorption by the M. oleifera seed coagulant for removing COD and TDS in a leachate was 84.5 and 82.6 %, respectively, and obtained at an optimum dosage of 100 mg L^{-1} . Based on the results obtained from the kinetic models, the equilibrium data were best fitted with the Elovich kinetic model than that of other models, because Elovich kinetic model at different physico-chemical conditions showed very high correlation coefficients ($R^2 = 0.993$ for COD and $R^2 = 0.996$ for TDS). Thus, the results of this study indicate that use of M. oleifera coagulant for removing COD and TDS in a municipal solid waste leachate seems to be an economical and worthwhile alternative over other conventional methods, because of their abundant source, low price, multi-purposes, biodegradation, better coagulation and antimicrobial properties.

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