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PURIFICATION OF AUTOMOBILE WASTEWATER USING FLY ASH-CLAY COMPOSITE

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ABSTRACT. The adsorbent Fly ash-clay composite was tested for the treatment of automobile service station wastewater. Batch experiments were conducted to determine optimum fly ash to clay ratio, kinetic data and adsorption isotherms. 2:1 fly ash to clay ratio was obtained with the highest adsorption capacity. Adsorption kinetics were best fitted into Pseudo second order kinetic model giving a theoretical adsorption capacity of 156.25mg/g. Equilibrium data were fitted into Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms. Experimental data was best fitted to Langmuir adsorption isotherm showing a favorable adsorption.

1. INTRODUCTION

Wastewater effluent from most of automobile service stations are usually discharged to the environment without considering the regulatory limits set by Central Environmental Authority (CEA) in Sri Lanka because of not having centralized system to treat effluent prior to discharge. Biological Oxygen Demand (BOD), Chemical Oxygen demand (COD) and oil and grease content in the effluent has a significant variation from the required values. This research focused on removing COD and oil and grease content up to acceptable discharge quality. The available treatment methods are categorized under physical, chemical

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and biological treatment methods. Filtration and gravity settling are physical methods which cannot remove chemicals from wastewater. Because of the pre-treatment required, membrane separation is identified as an expensive technique. Coagulation is not economically feasible in Sri Lanka because it involved with filtration prior to coagulation and neutralization afterwards. Adsorption is identified as the economically feasible method for treating automobile wastewater compared to other expensive methods such as coagulation or membrane separation by developing a low cost readily available adsorbent. Fly ash from Norochcholai power plant was selected as the adsorbent because of the availability and adsorption capacity. Clay was added to fly ash as the binding agent to make pellets because fly ash itself will result in low flow rates in a fixed bed column application due to its fineness. Results for the adsorption using fly ah-clay composite was carried out batch wise which can be used in future work for fixed bed column experiments.

2. LITERATURE REVIEW

Literature review was conducted considering three different aspects as research works carried out on automobile wastewater treatment, usage of fly ash-clay in adsorption process and usage of adsorption columns in wastewater treatment. Automobile service station wastewater have been mainly treated based on coagulation, filtration and biodegradation. Coagulation was considered as the low cos treatment method for automobile service station wastewater. Coagulation can be used to remove oil and grease in wastewater by characterizing COD, total solids, total suspended solids and oil and grease where no attention towards removing contaminants as COD [1]. Bio degradable surfactants, oil and grease in automobile wastewater was removed using bacteria known as P.aeruginosa where maximum degradation of 50Fly ash have the capability to remove COD and BOD level in wastewater [5] Porous honeycomb structure of fly ash make the large surface area increasing the adsorption capacity [6]. Coal Fly ash can be modified using HCL and FCl3 to increase the surface properties. Clay increases the surface properties of fly ash as a binding agent [7].

3. METHODOLOGY

3.1. **Preparation of Fly Ash-Clay Pellets.** Fly ash and clay were weighed to pre-determined ratios and mixed with water. Small pellets were made using a normal syringe and kept for air drying for 24 hours. Then pellets were kept in a muffle furnace at 550oC for 30 minutes for heat treating. Heat treating increased the bonding between fly ash and clay otherwise pellets would disintegrate when added to water.

3.2. **Preparation of Synthetic Wastewater Sample.** Oil and grease content of actual wastewater sample was measured using Separatory Funnel Method, which was 2619.5 mg/L. Therefore, 3g of selected engine oil (5W30) were added to 1L of normal tap water samples. Different weights car wash liquid was added to them and COD were measured. Actual wastewater sample had a COD level of 2132.48 mg/L and amount of car wash liquid should be added was determined by extrapolating the COD values of measured samples, which was 7g for 1L of water.

3.3. **Characterization of Pellets.** Surface morphology was characterized using Scanning Electron Microscope (SEM) and functional groups present in the pellets were characterized using Fourier Transform Infra-Red Spectroscopy (FTIR). SEM images were taken at 1K, 2K and 5K magnification but 5K. FTIR showed a peak range between 4000-600 cm-1 and transmittance spectroscopy was used.

3.4. **Optimum Fly Ash to Clay Ratio.** 10g of pellets prepared with 1:2, 1:1, 2:1 fly ash: clay ratio was added to 500 mL of synthetic sample. Samples were agitated at 30 rpm for 30 minutes at room temperature and original pH value (6.1). Final COD was measured after 30 minutes and initial COD was measured using a blank sample. Pellets with optimum ratio found were used for other experiments.

3.5. **Effect of Contact Time.** 10g of pellets were added to 500 mL of synthetic wastewater samples and agitated at 30 rpm. Samples were withdrawn after 30, 60, 90, 120, 150 and 180 minutes for measuring COD. Blank was used to measure initial COD level and experiment was done at room temperature and 6 pH. Results were used to analyze kinetic data.

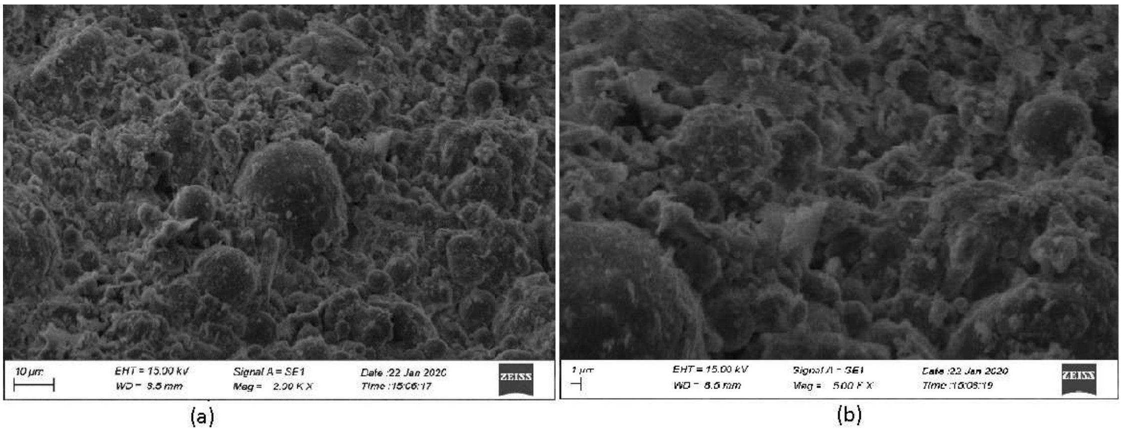

FIGURE 1. SEM Image of Pellets At (A) 2K Magnification (B) 5K Magnification

3.6. **Effect of Initial COD level.** Synthetic wastewater samples with different initial COD levels were prepared by adding different weights of oil and car wash liquid to the water. Ratio between engine oil to car wash liquid was kept constant (3:7). 10 g of pellets were added to each 500 mL sample and agitated at 30 rpm for 3 hours which was the time required to reach equilibrium stage. Experiment was done at room temperature and 6 pH. Both initial COD and final COD values were measured. Obtained data were used to analyze adsorption isotherms.

3.7. **Effect of pH level.** pH level of synthetic wastewater samples were adjusted to 3, 5, 7, 9 and 11 using HCL and NaOH solutions. 10 g of pellets were added and agitated at 30 rpm for 30 minutes. Experiment was done at room temperature. Both initial and final COD levels were measured.

4. RESULTS AND DISCUSSION

4.1. **Characterization of Pellets.** SEM (Scanning Electron Microscope) images in Figure 1 clearly show that spherical fly ash particles and cluster type clay particles are bounded together due to heat treatment. Rough surface indicates high capacity for adsorption due to increased pores.

FTIR results as mentioned in Figure 2 shows strong Si-Al-O bonds at 1054 cm-1 due to use of both fly ash and clay. Between the range 2700- 3400 cm-1, presence of C can be identified mainly due to unburnt C in coal. Between 3650-3700 cm-1, O-H bonds are present due to trapped water molecules inside the

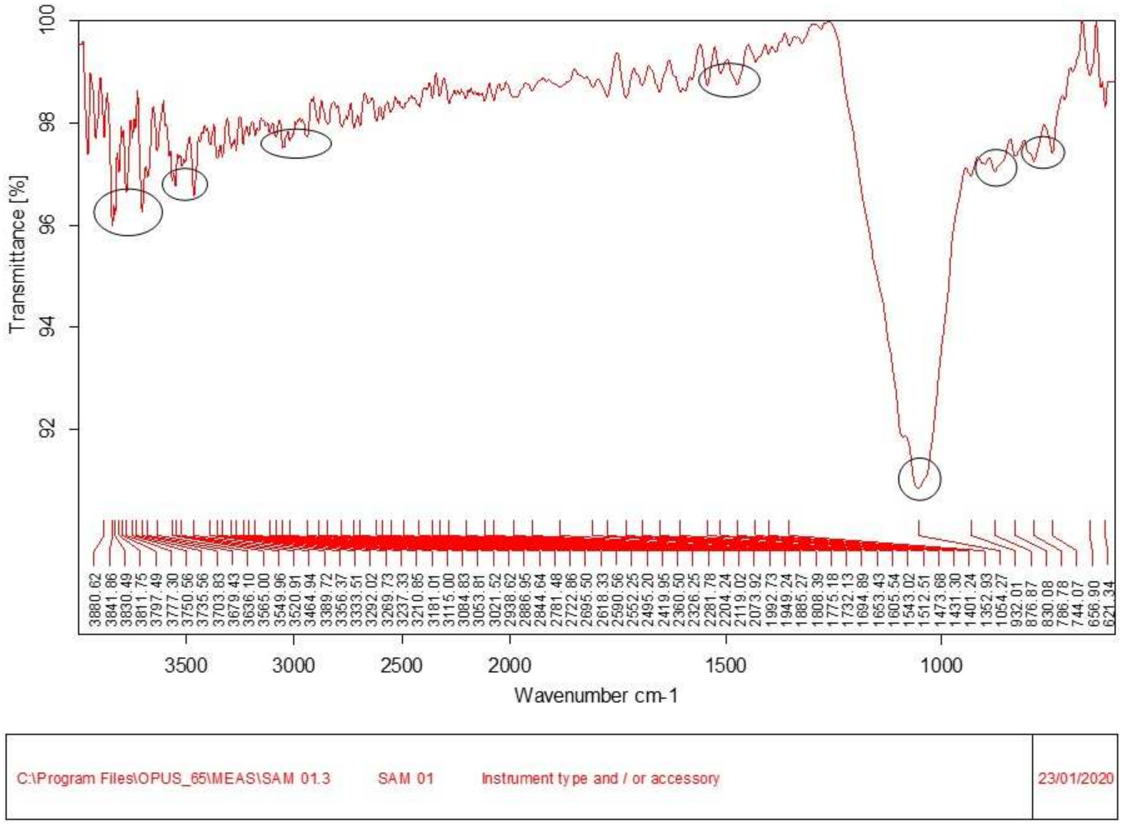

FIGURE 2. FTIR Results of Pellets

Table 1- FTIR Frequency Range and Functional Groups Present In the Sample

Frequency range (cm^{-1})	Functional group
744	Al-O vibration
787	Valance band of Si-O-Al
1054	Si-O-Al bonding
1605-1352	Si-O stretching
2938-2722	C-H stretching
3356-3269	C unsaturated bonding
3679-3659	O-H bonding

pellets. Al-O vibrations and Si-O-Al valance bands can be observed in the range 700-800 cm-1.

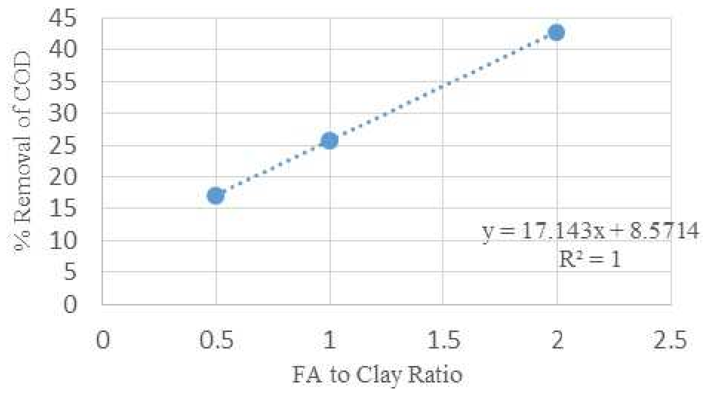

FIGURE 3. % Removal of COD vs. Fly Ash: Clay

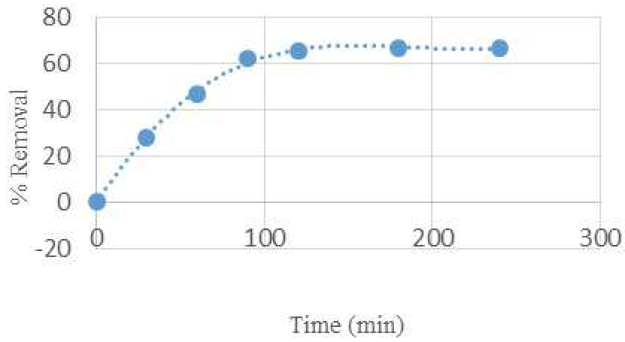

FIGURE 4. % Removal Of COD Vs. Contact Time

4.2. **Optimum Fly Ash to Clay Ratio.** Percentage reduction of COD was increased linearly with the fly ash to clay ratio used i.e. higher the fly ash amount used, higher will be the COD removal. However, integrity of pellets will be reduced when lower clay amounts are used thus 2:1 was selected as the optimum fly ash: clay ratio for further experiments.

4.3. **Effect of Contact Time.** Experimental results (Fig.4) shows that rate of adsorption is declining with time and net adsorption becomes zero after approximately 150 minutes. It indicates that system has been reached equilibrium. Equilibrium percentage removal of COD was measured as 67.19%.

4.4. **Effect of Initial COD Level and pH Level.** Both initial COD level and pH level do not show a strong relationship in terms of percentage removal of COD. Up and down variation was observed in both cases. However, percentage

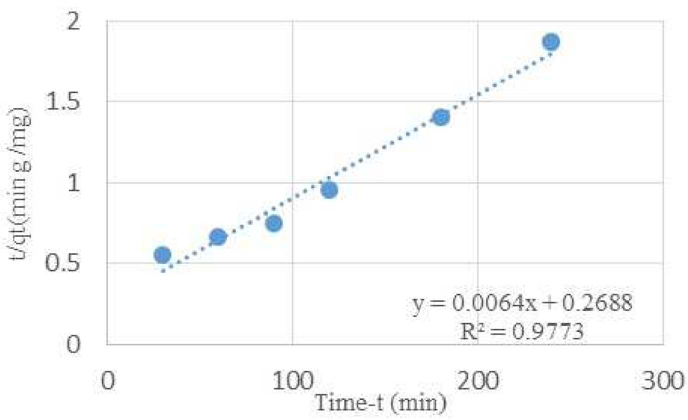

FIGURE 5. Pseudo Second Order Kinetic Model

removal is higher when initial COD level is lower and maximum percentage removal was observed at neutral pH level.

4.5. **Adsorption Kinetics.** Data driven from contact time experiment was fitted into Pseudo first order kinetic model and Pseudo second order kinetic model. As shown in Fig.5, Pseudo second order model showed the highest R2 value which is 0.9773 thus it was selected as the kinetic model of the adsorption. Under Pseudo second order model, Maximum Theoretical Adsorption Capacity was 156.25 mg/g (mg of COD per 1g of adsorbent) and Adsorption Rate Constant was 1.524 x 10-4. Actual Adsorption Capacity was obtained using experimental data as 128.36 mg/g.

4.6. **Adsorption Isotherms.** Data obtained from Effect of Initial COD Level experiment was fitted to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherm models. Each model showed R2 values of 0.943, 0.909, 0.665 and 0.637 respectively. Therefore, Langmuir isotherm model was selected as the Adsorption Isotherm Model for the adsorption process. Calculations related to Langmuir Model shows a Maximum Monolayer Coverage Capacity of 101.01 mg/g and a Langmuir Adsorption Constant of 5.455x10-4 L/mg. Separation Factor (RL) is 0.6866 which indicates a favorable adsorption.

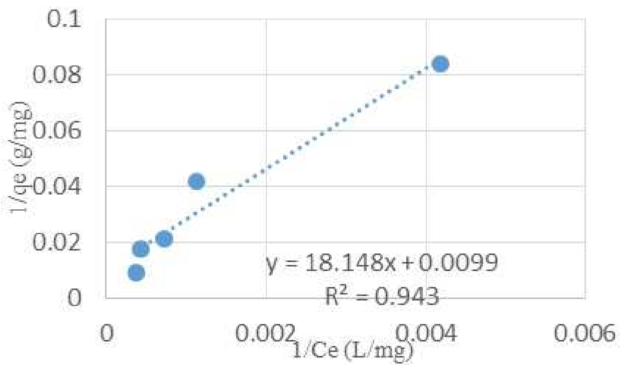

FIGURE 6. Langmuir Adsorption Isotherm Model

5. CONCLUSION

Experiments that have been carried out show that fly ash-clay composite pellets can reduce COD levels considerably in automobile wastewater. Percentage removal can be increased by increasing fly ash amount. Kinetic data fits into Pseudo Second Order Model and isotherm data best fits into Langmuir Isotherm Model. Experimental maximum adsorption capacity was found as 156.25 mg/g.

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