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 establish the adsorption column parameters which were 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 kinetics data were fitted into Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms. Experimental data were best fitted to Langmuir adsorption isotherm showing a favorable adsorption.

Key words: Fly ash; Adsorption; Automobile; Wastewater

INTRODUCTION

Wastewater effluents from most automobile service stations are usually discharged into the environment without considering the regulatory limits set by Central Environmental Authority (CEA) in Sri Lanka because of not having a centralized system to treat effluent prior to discharge. BOD, 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 the acceptable discharge quality.

The available treatment methods are categorized under physical, chemical and biological treatment methods. Filtration and gravity settling are physical methods which cannot remove chemicals from wastewater. Because of the pretreatment 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 column application due to its fineness. Even though only batch experiments were carried out. These data can be used in future work for adsorption column experiments.

METHODOLOGY

Preparation of Fly ash-Clay Pellets

Fly ash and clay were weighed to predetermined 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 550^{o}C for 30 minutes for heat treating. Heat treating increased the bonding between fly ash and clay. Otherwise pellets would disintegrate when added to water.

Preparation of Synthetic Wastewater Sample

Oil and grease content of an 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 of car wash liquid were added to them and COD were measured. The actual wastewater sample had a COD level of 2132.48 mg/L and the amount of car wash liquid which should be added was determined by extrapolating the COD values of measured samples, which was 7g for 1L of water.

Characterization of Pellets

Surface morphology was characterized using Scanning Electron Microscope (SEM) and the 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.

Optimum Fly ash to Clay Ratio

10g of each pellet 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 found with optimum ratio were used for other experiments.

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 6.1 pH. Results were used to analyze kinetic data.

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 6.1 pH. Both initial COD and final COD values were measured. Obtained data were used to analyze adsorption isotherms.

Effect of pH Level
pH levels 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.

RESULTS AND DISCUSSION

Characterization of Pellets
SEM images (Figure 01) 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.

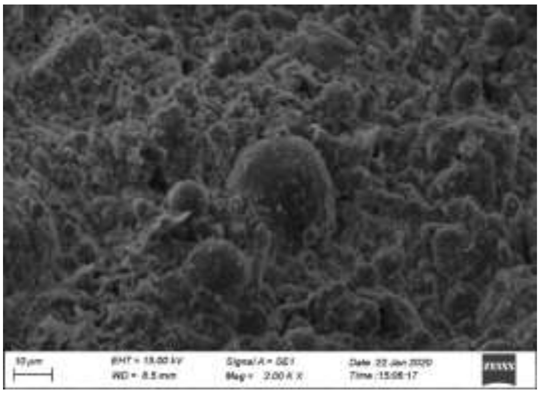

Figure 1. SEM Image of pellets at 2K magnification

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

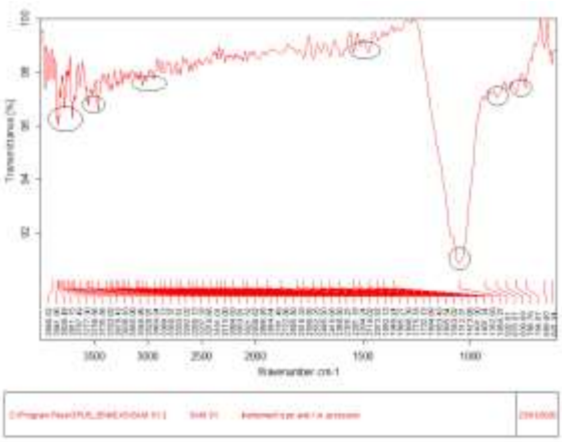

Figure 2. FTIR results of pellets

Optimum Fly ash to Clay Ratio
Percentage removal 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.

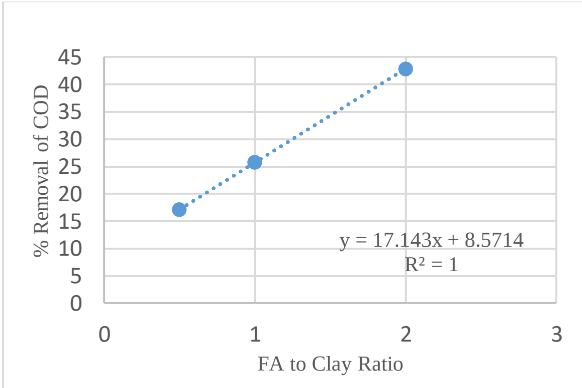

Figure 3. % Removal of COD vs FA: Clay

Effect of Contact Time
Experiment 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%.

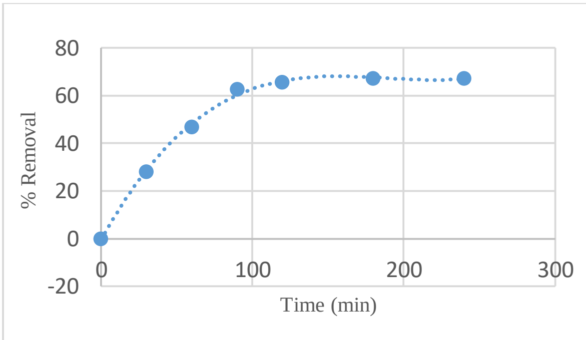

Figure 4. %Removal of COD vs Contact Time

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

Adsorption Kinetics

Data derived from contact time experiment was fitted into Pseudo first order kinetic model and Pseudo second order kinetic model. Pseudo second order model showed the highest R^2 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.

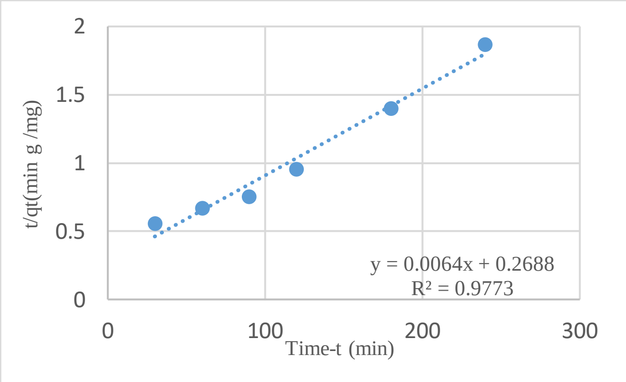

Figure 5. Pseudo Second Order Kinetic Model

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 R^2 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 5.455×10^{-4} L/mg. Separation Factor (R_L) is 0.6866 which indicates a favorable adsorption.

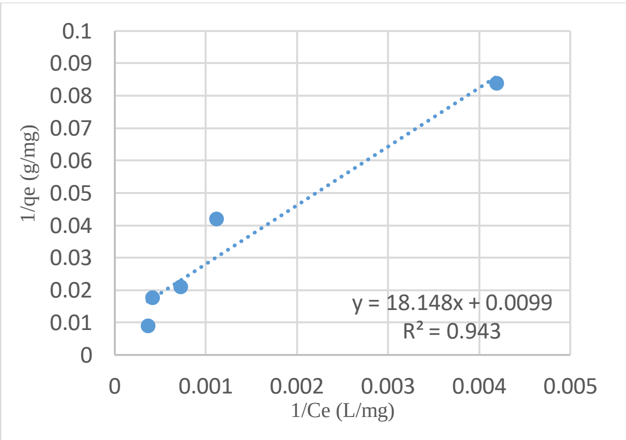

Figure 6. Langmuir Adsorption Isotherm Model

CONCLUSION

Experiments carried out show that fly ash and clay 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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