

LACTIC ACID REMOVAL FROM WASTEWATER BY USING DIFFERENT TYPES OF ACTIVATED CLAY

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ABSTRACT

Different treatment techniques; based on physical, chemical or biological processes, are used in the removal of organic pollutants from wastewater streams. One of the widely used physical processes is the adsorption process using activated carbon. A modified process utilizing a combined activated carbon-clay mixture was adopted in the present study providing improved efficiency.

The present work investigated the effect of the acid and alkali activated clay on the removal efficiency of lactic acid from a wastewater stream. Acid activated clay resulted in improved efficiency (120%) compared with alkali activated clay. The efficiency of removal increased with increasing the contact time, decreasing the initial pollutant concentration and increasing the solid to liquid ratio. The use of air circulation resulted in an increase in the rate of adsorption since the adsorption process is exothermic.

It was also observed that the concentration of microorganisms produced increased as the process is left for an extended period of time. Finally, it was found that the Freundlich isotherm successfully described the adsorption process at all conditions while the Langmuir isotherm described the process only at low concentration of activated clay.

Keywords: wastewater treatment, activated clay treatments, acid and alkali activated clay, organic waste adsorption and lactic acid removal.

INTRODUCTION

The increasing occurrence of many synthetic and natural organic substances in natural water led to the importance of using the adsorption technique as one of the most effective methods of removing impurities from wastewater. Activated carbon and clay are among many different adsorbents used in this technique ^[1].

The use of clay has some advantages over activated carbon. Clay can remove approximately 70% of the waste of water in a water removal system and that the remainder 30% can be removed using activated carbon. The main disadvantages of using activated carbon and which make of the use of clay a better choice are the following: (1) Its limited natural resources, (2) It must be disposed off, (3) Its regeneration is expensive.

Clay minerals^[2] are hydrous aluminosilicates with fine particle size; they are composed of two basic building blocks Silicon–Oxygen Tetrahedron (Si_2O_5)⁻² and Aluminum Octahedral (Gibbsite Sheet). Tetrahedral sheets are composed of individual tetrahedrons which share every three out of four oxygens. They are arranged in (*) hexagonal pattern with the basal oxygens linked and the apical oxygens pointing up/down. Octahedral sheets are composed of individual octahedrons that share edges composed of oxygen and hydroxyl anion groups with Al^{3+} , Mg^{2+} and Fe^{2+} typically serving as the coordinating cation. These octahedrons are arranged in a hexagonal pattern^[3].

The most common and most effective type of clay used in water purification is bentonite which is an adsorbent and is generally impure clay consisting mostly of montmorillonite^[4].

The structure of montmorillonite is a gibbsite layer sandwiched between two silica sheets to form the structural unit^[5]. The substitutions are mainly within the octahedral layer (Mg^{+2} , Fe^{+2}) and to a much less extent within the silicate layer ($\text{Al}^{+3}/\text{Si}^{+4}$).

Bentonites are usually composed mainly of montmorillonite, although some many consist of the rare clay minerals, i.e., beidellite, saponite, hectorite and nontronite.

The chemical composition of the clay mineral is based on a hydroxyl-aluminosilicate framework. The crystal structures of the clay minerals are formed by a combination of sheets of silica tetrahedral and alumino octahedral. Part of the trivalent Al is substituted by divalent Mg or Fe in some cases. In such cases, substitution is accompanied by addition of alkaline metals, such as Na and K or alkaline earth metals such as Mg and Ca to provide charge balance^[6].

The adsorption behaviour of organophilic bentonites in contact with aqueous solutions of organic compounds was studied by Stockmeyer^[7] Phenol, aniline, nitroethane, diethyl ketone, ethoxy acetic acid, maleic acid and hexadecyl pyridinium bromide were used as test substances. The investigated organoclays vary in the degree of their total CEC exchanged by organic counter-ions.

Juang et al^[8] studied the ability of activated clay for the adsorption of dyes from aqueous solutions. They used a low-cost inorganic acid-activated clay as adsorbent for adsorption of six dyes (two basic, one acidic, one disperse, direct and reactive dyes). The equilibrium data could be well described by the Langmuir equation.

Organic compounds derived from agricultural, industrial and domestic waste frequently contaminate soil and ground water. Any attempt to estimate the effect of these organic acids on water quality must include the various interactions between the organic material and the minerals of the host rock and soil. Jiwchar et al ^[9] studied the effect of kaolinite surfaces on the degradation rate of oxalate in the presence of microorganisms.

A method was tested by Espantaleón et al ^[10] to reduce the pollution of effluents produced in the hide transformation process. Adsorption processes with clays could constitute a simple, selective and economical alternative to conventional physical–chemical treatments. The adsorption capacity of natural and acid-activated bentonite and sepiolite for anionic dyes normally used in the tannery was compared with that of a conventional adsorbent such as activated carbon.

Currently, water pollution represents a great challenge, and activated carbon is a common adsorbent used to remove hazardous contaminants. Unfortunately, it is a non-selective process. The main object of the study presented by Hocine et al ^[11] was the use of montmorillonite clays, which can offer both an alternative and a selective process. The adsorption measurement of p-aminobenzoic acid on montmorillonite clays showed a real potential for removing hazardous contaminants in waste such as pesticides and chlorophenols. The results showed that the determination of aromatic amines remained dependent on some parameters such as pH, temperature and aqueous concentrations.

Two organobentonites (ODTMA-B, HDTMA-B) were synthesized by Nuray et al ^[12] using hexadecyltrimethyl ammonium bromide (HDTMAB) and octadecyltrimethyl ammonium bromide (ODTMAB). Synthesized organobentonites were characterized by X-ray diffraction, particle size distribution, and surface area analysis.

The ability of bentonite to remove malachite green from aqueous solutions was studied by Tahir and Naseem ^[13] for different adsorbate concentrations by varying the amount of adsorbent, temperature, pH and shaking time. Adsorption technique was applied by Taher and Naseem ^[14] for the successful removal of Cr(III) from tannery wastewater. For this purpose, wastewater samples were collected from 18 tanneries to determine the actual concentration of Cr(III) present in the influent (chrome tanning stage) and the combined wastewater.

Removal of copper (Cu^{2+}) and zinc (Zn^{2+}) from aqueous solutions was investigated by Veli and Alyüz ^[15] using bentonite, a natural clay. During the removal process, a batch technique was used, and the effects of pH, clay amount, and heavy metal concentration and agitation time on adsorption efficiency were studied. Langmuir and Freundlich isotherms were applied in order to determine the efficiency of natural clay used as adsorbent.

Removal of lactic acid from waste water was investigated in this work using alkali and acid activated clay. During the removal process, a batch technique was used, and the

effects of contact time, clay amount, and lactic acid concentration, rate of stirring, temperature and aeration on adsorption efficiency were studied. Two isotherms were tested to determine which isotherm the adsorption processes follow. Finally, the effect of removal overnight through 2, 5 and 7 days were studied, and the formed biomass expressed as mixed liquor volatile suspended solids were then calculated.

EXPERIMENTAL METHODS

The batch adsorption systems were operated in a one liter beaker filled with the wastewater (water + lactic acid). The initial COD was measured using the digestion reactor and spectrophotometer technique. Different amounts of alkali and acid activated clay were used. Amounts of 2, 4, 6 and 8g were added to the wastewater samples at ambient temperature, the mixture was agitated for 40 minutes with continuous stirring until the adsorption was complete. Thorough mixing promotes good contact between the clay and liquid and increases the reaction rate. A sample was left to settle and was filtered using. The filtrate samples were put in a digestion reactor for 2 hours at 150°C. The digested filtrate was cooled to ambient temperature, and the final COD was measured using a spectrophotometer.

The experimental work was divided into three parts; in the first part the effect of removal using alkali activated clay was investigated. Variables investigated were the following: the effect of removal time on lactic acid, the amount of alkali activated clay on lactic acid, the concentration of lactic acid on the organic removal capacity, the effect of stirring on lactic acid removal, the effect of temperature on lactic acid removal, the effect of aeration on lactic acid removal. The different adsorption isotherms were tested to identify which one describes best the adsorption process.

In the second part, the effect of removal using acid activated clay was studied. The parameter investigated was the effect of solid to liquid ratio (acid activated clay to lactic acid). The different adsorption isotherms were tested to identify which one describes best the adsorption process.

Finally the third part was concerned with the determination of Biomass in the form of (MLVSS)^[16].

RESULTS AND DISCUSSION

Figure **Error! Reference source not found.** shows a typical experimental curve where COD decreases as time increases due to the adsorption of lactic acid molecules on alkali activated clay, that capacity of alkali activated clay and ability to adsorption decrease till it reaches almost constant value to give approximate straight line. This straight line is corresponding to time value needed to reach equilibrium, and this was taken to be constant in all the remainder of experiments.

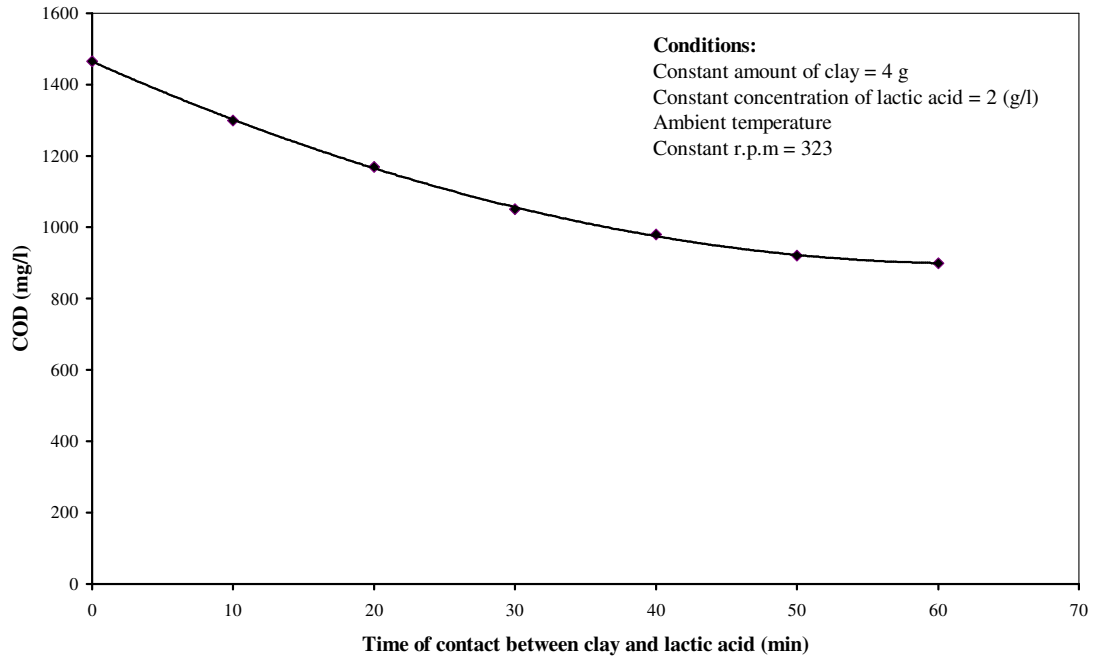


Figure 1. A typical experimental adsorption curve

Figure 2 Shows the effect of amount of alkali activated clay on the lactic acid removal, with increasing amount of alkali activated clay the COD will decrease for the solution at constant concentration of lactic acid and percentage removal will increase with increasing the amount clay. This behavior is expected since increasing of amount of alkali activated clay increases the area available for adsorption and more of the organic compound is removed.

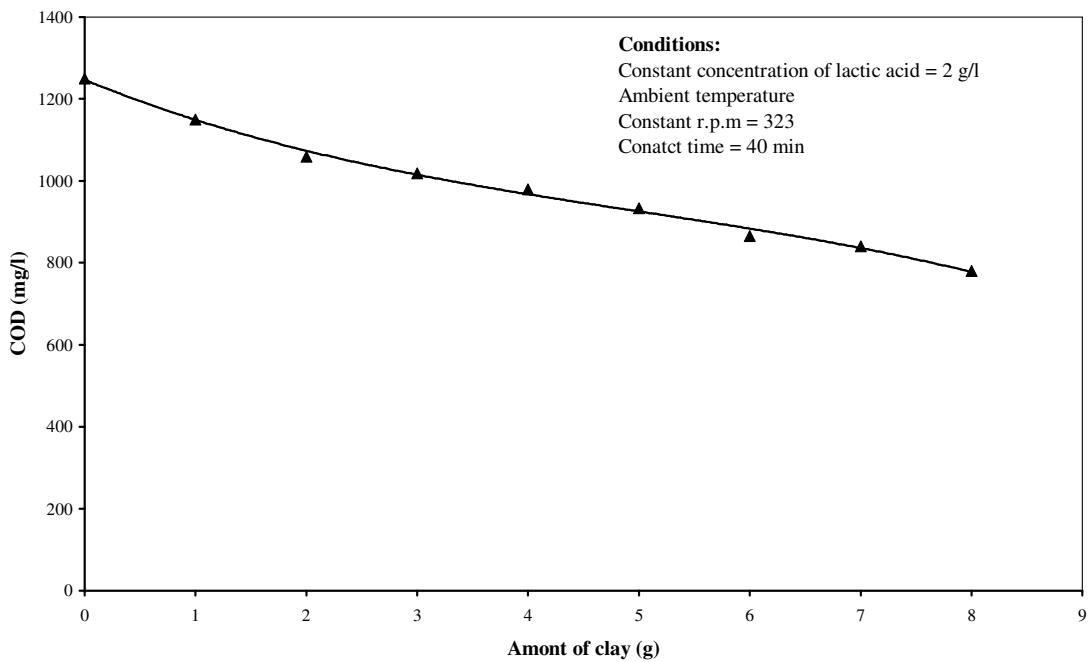


Figure 2. The effect of increasing the amount of clay on the adsorption of lactic acid

Figure 3 shows the effect of solid to liquid ratio which increases with increasing waste concentration at constant amount of alkali activated clay. At the same time, COD decreases with increase amount of alkali activated clay at constant concentration of the waste. Also the percentage removal decreases with increasing of concentration of waste at constant amount of alkali activated clay. It will be the largest value at first, and then it decreases. This is an expected observation since constant amount of alkali activated clay has a given capacity, and this capacity increases with increasing clay and not with concentration of organic waste. The relationship is represented by almost straight line. This is an indication of the constant capacity of clay for the adsorption of lactic acid on its surface.

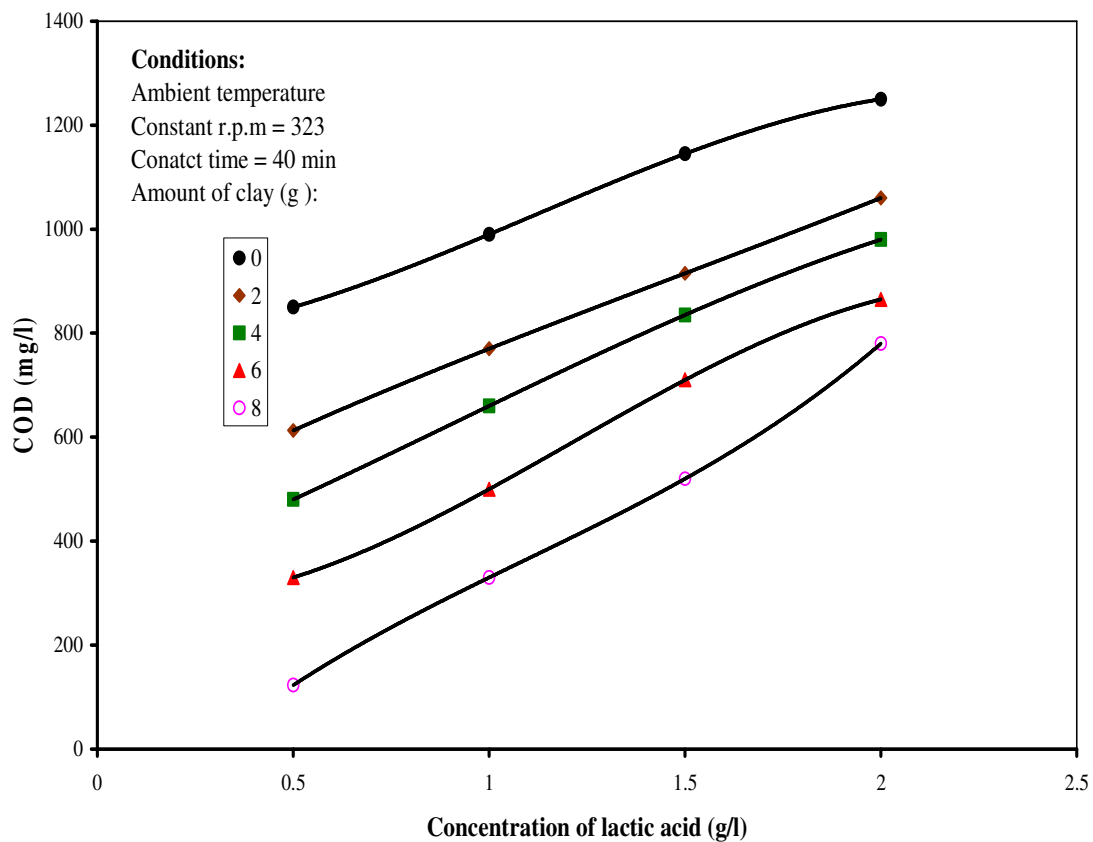


Figure 3. The COD of solution as a function of initial lactic acid concentration using different amounts of clays

As the rpm increases, the rate of adsorption decreases and the COD of solution increase. This effect is shown in Figure 4, increasing the rate of stirring highly reduces the boundary layer effect on the adsorption process. As it goes up, the prevailing controlling mechanism is the diffusion through the solid alkali activated clay which is a slow process also since adsorption is physical in nature it can be assumed that with increasing stirring the weakly adsorbed compound will be easily desorbed from the surface. This view may explain the effect of increasing the rpm on the adsorption process.

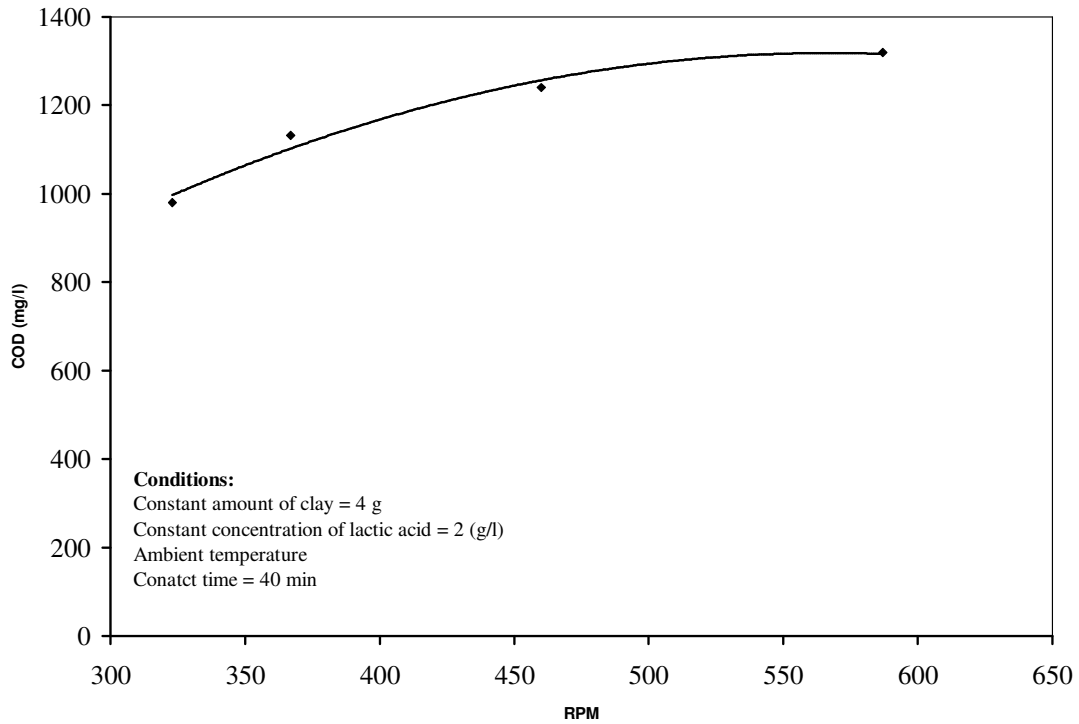


Figure 4. The effect of rpm on the adsorption of lactic acid on alkali activated clay

Figure 5 shows COD increasing with increasing temperature at a constant concentration of waste and using constant amount of alkali activated clay. This shows that the adsorption process is exothermic in nature ^[17].

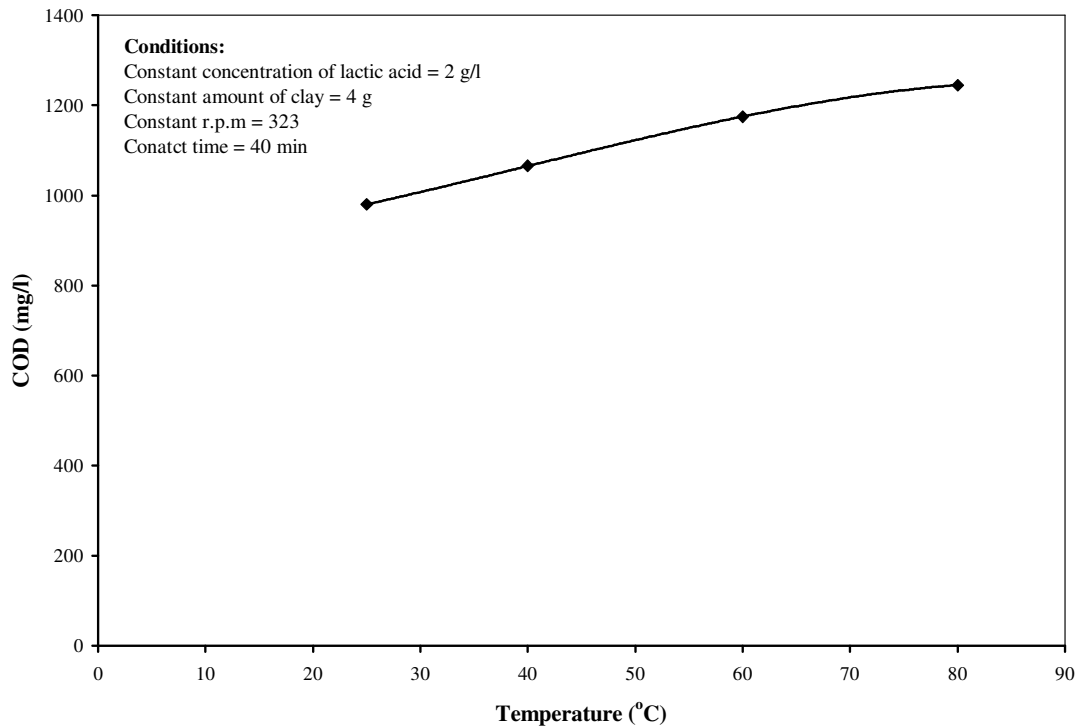


Figure 5. The Effect of temperature on the adsorption process

The effect of aeration on the removal of the organic compound by clay was investigated in a series of experiments. The results obtained are presented in Figure 6 which shows that the adsorption process proceeds faster in the presence of air. Aeration disturbs the boundary layer and increases the rate of mass transfer from the bulk to the surface of solid, thus increasing the rate of adsorption of lactic acid on the surface of alkali activated clay.

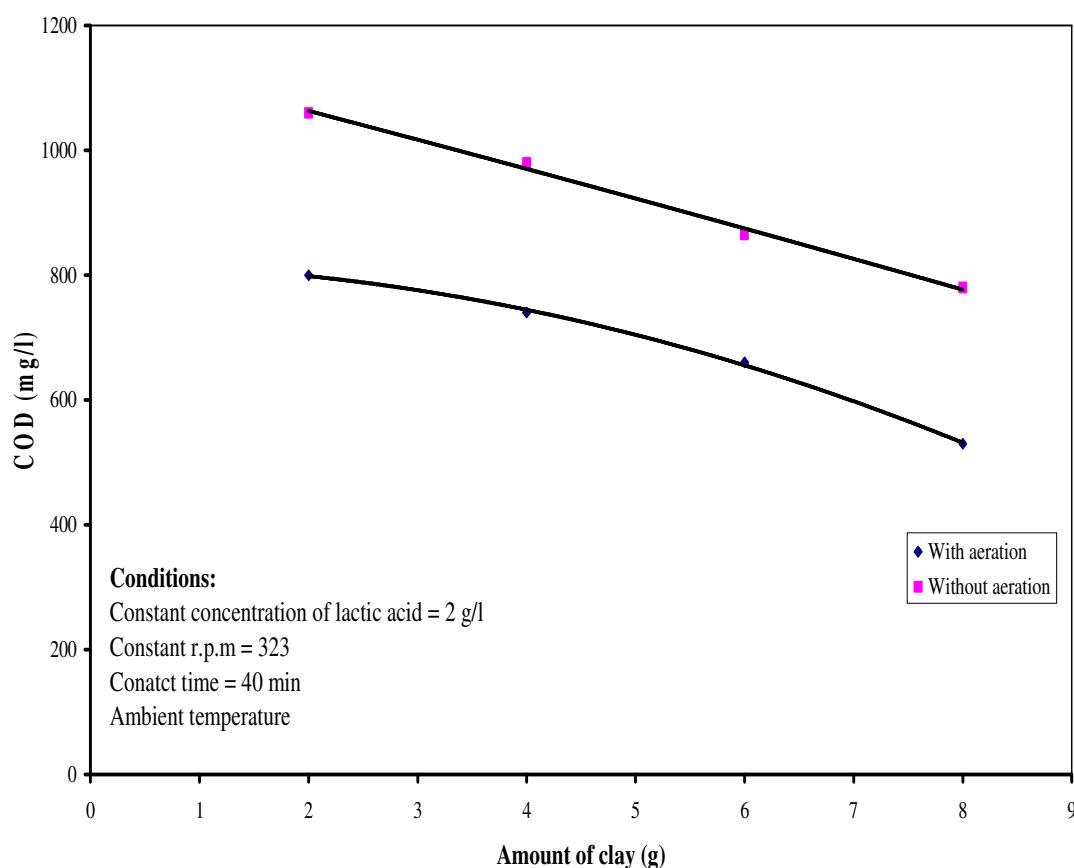


Figure 6. The COD of solution as a function of amount of clay with and without Aeration

Figure 7 shows that acid activated clay is more effective than the alkali activated one. With acid activated clay, the structure of clay is more open with higher ion exchange capacity than the alkali activated clay. Also in acid activated clay the presence of hydrogen ions instead of alkaline (OH) ions, which have highly sorption capacity^[4], increase the ability for adsorption.

In a series of experiments, the adsorption isotherms of the lactic acid were investigated. The results obtained were tested to find which isotherm it follows. It was found that the adsorption process fits the Freundlich isotherm for all concentrations and under all experimental conditions. Figure 8 shows the result of plotting $\log(x/m)$ against $\log C_e$ for experiments carried using alkali activated clay. The straight line obtained proves that the adsorption process follows Freundlich equation.

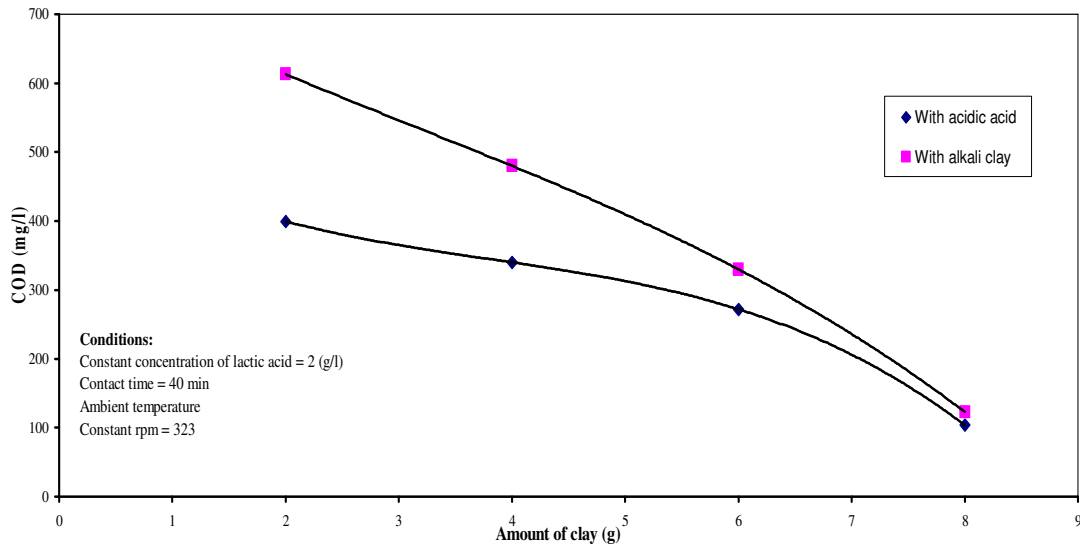


Figure 7. The COD of solutions as a function of amount of clay for two types of activated clays

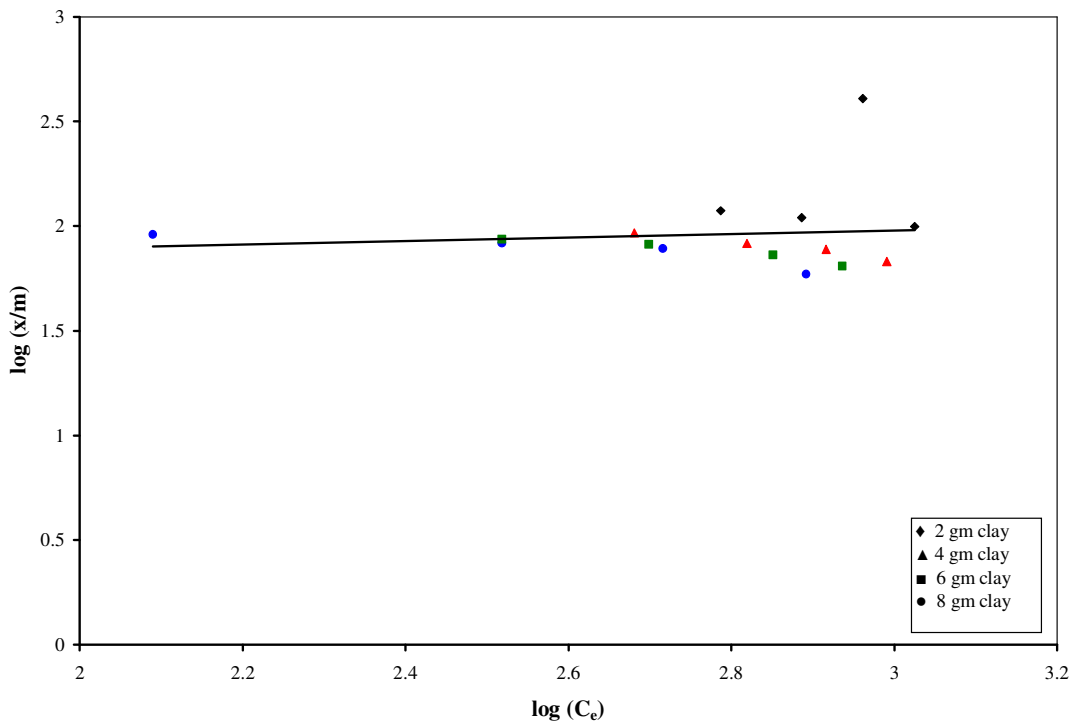


Figure 8. The adsorption isotherm for lactic acid with alkali activated clay (Freundlich Isotherm) $\log (x/m) = 0.15884 \log C_e + 1.903896$

Furthermore, it was found that at low amount of alkali activated clay 2g, the results also satisfy the Langmuir isotherm. Figure 9 represents this behavior.

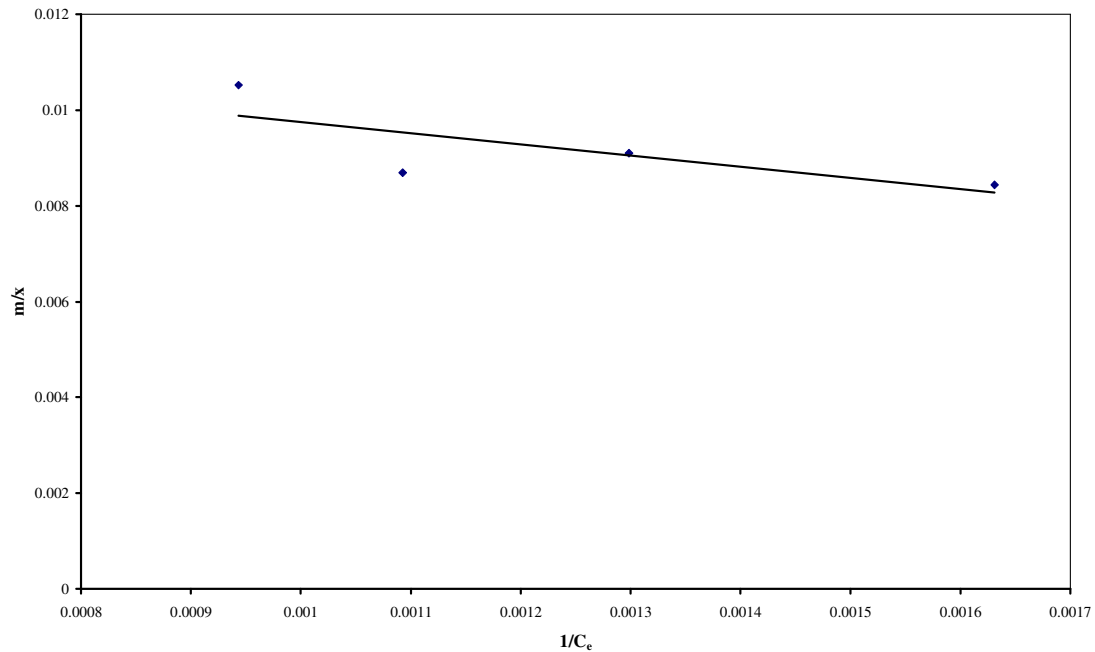


Figure 9. The adsorption isotherm for lactic acid with 2 g alkali activated clay (Langmuir Isotherm)

For acid activated clay, results for lactic acid are given in Figures 10 and 11. The same behavior was observed as the case of alkali activated clay. The results obtained are in agreement with the work of Juang et al ^[8] studied, Nuray et al ^[12], Tahir and Nasseem ^{[13],[14]} and Veli and Alyüz ^[15]. These authors reported that their data were represented by Langmuir isotherm ^[8] and with Langmuir and Freundlich isotherm ^[13,14].

The effect of aeration on the removal of the lactic acid with clay was investigated in a series of experiments during five days through over night. The results obtained are presented in Figure 12. This figure shows a marked decrease in the COD of solution as time progresses. It was observed that a biomass was formed and the removal of the organic waste is mainly due to bacterial action. The process becomes similar to the activated sludge process used in wastewater treatment of industrial waste.

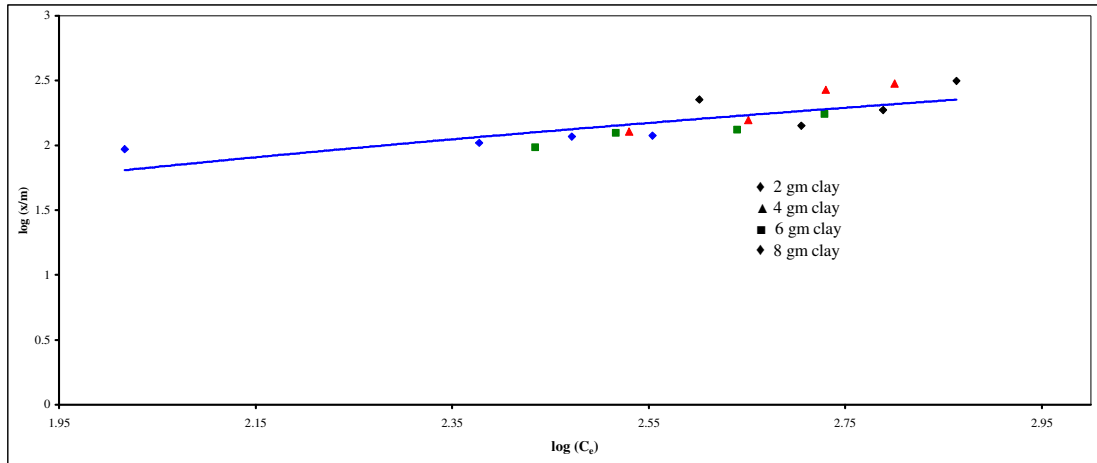


Figure 10. The adsorption isotherm for lactic acid with acid activated clay (Freundlich Isotherm) $\text{Log } (x/m) = 0.658 \text{ log } C_e + 1.567885$

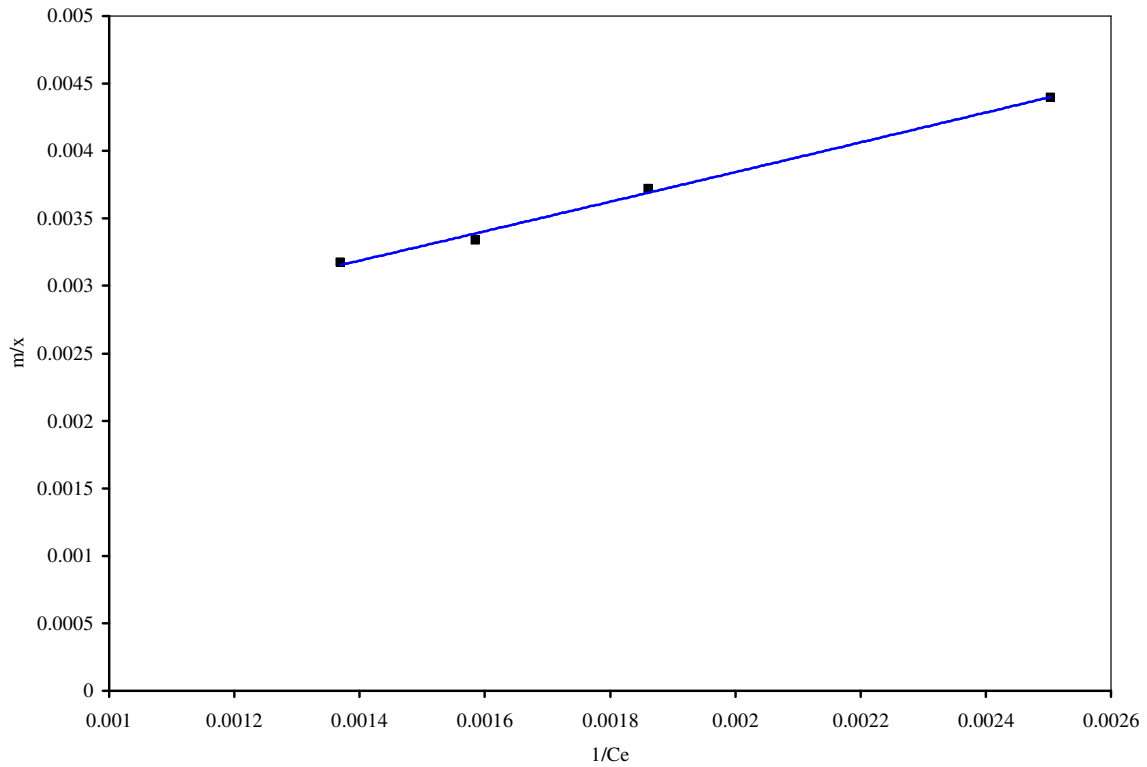


Figure 11. The adsorption isotherm for molasses with 2 g acid activated clay (Langmuir Isotherm)

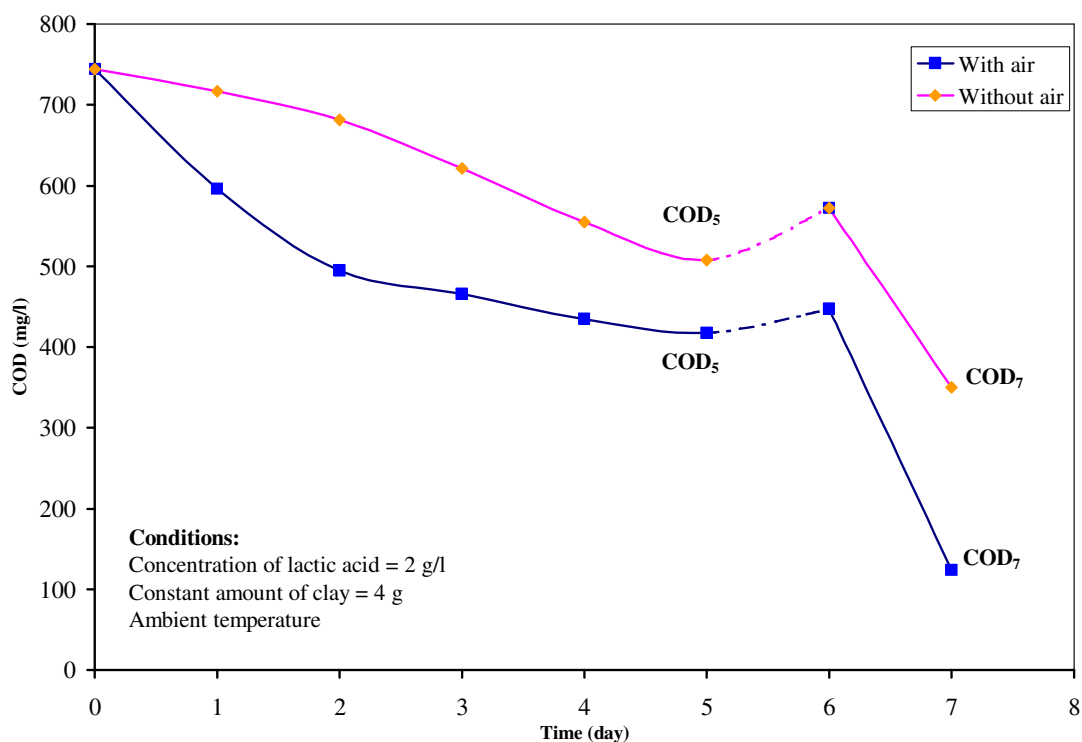


Figure 12. The COD of solution in 5 and 7 days with and without aeration for lactic acid

CONCLUSIONS

From the present investigations, the adsorption process is made of main steps. These are diffusion through the boundary layer to the surface of solid particle, and sorption of the diffused ions on the surface of solid and forming an adsorbed layer on the solid. The more porous the structure of the solid the more is the amount adsorbed. Activated clay has a porous structure as it is formed of layers of silicates connected together by ions^[2]. The adsorption process takes place readily on the activated clay because of such structure. The amount of compound removed is increased with increasing the amount of clay. Also, the higher the initial concentration the higher the residual concentration in solution after the adsorption is complete. The results obtained showed the adsorption process is physical in nature as it is discussed by the Freundlich and Langmuir isotherms. While Freundlich described the adsorption process at all the different conditions, it was found that Langmuir described the process at low concentration of clay.

This is in agreement with the results of Juang et al^[8], Nuray et al^[12], Tahir and Nasseem^[13,14], and Veli and Alyüz^[15] who reported that the adsorption process follows both the Freundlich and Langmuir isotherms.

This behavior may be because at low concentrations of clay, the monolayer is formed while at high concentration the interaction between solid particles hinders the monolayer formation. It was also found that the adsorption process is not favored by

high temperature. This also confirms the physical nature of adsorption as it shows that the process is exothermic process^[17].

It was observed that when leaving the solution for more than one day with and without aeration the COD decreased and bacteria have resulted. The produced microorganisms increased in quantity as the experiment was extended. It is observed that the experiment with passage of air gave better removal of lactic acid; the decrease in the COD is attributed to the effect of biomass or bacteria, and not due to the adsorption of the surface of the solid.

List of Symbols

C_e	concentration of solute remaining in solution
COD	Chemical Oxygen Demand (mg/l)
m	mass of adsorbent (g)
MLVSS	Mixed Liquor Volatile Suspended Solid
rpm	Revolution per Minute
x	amount of solute adsorbed (g)

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