# DEALCALIZATION OF SOUTHERN CIANJUR BENTONITE USING AMMONIUM HYDROXIDE AND CITRIC ACID

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***ABSTRACT***

*Dealcalization of southern Cianjur bentonite has been done to improve bentonite quality by reducing the alkali element (Na and Ca) content as impurities. The experiment used ammonium hydroxide and citric acid. The reaction parameters such as particle size, solution concentration, percent solid, time and contact temperature were optimized. Results of dealcalization using ammonium hydroxide obtained the optimum condition at particle size of -200+325 mesh, concentration of 4 N, percent solid of 10%, contact time of 36 hours and temperature of 100$^{o}$C with recovery as much as 32.55% for Na and 29.14% for Ca. Meanwhile, dealcalization using citric acid, got optimum condition at particle size of -325 mesh, concentration of 2N, percent solid of 10%, contact time of 24 hours, temperature of 100$^{o}$C with recovery as much as 33.01% for Na and 30.07% for Ca. The results also showed that both solutions gave better recovery for Na rather than for Ca. In conclusion, experiment using citric acid was better than using ammonium hydroxide as demonstrated by its higher recovery of alkali elements. However, results of this work have not met the standards of bentonite for catalyst hydrocarbon cracking.*

## 1. INTRODUCTION

Bentonite is a term used in trade for clay-containing 85 % of montmorillonite that resulted from tuff weathering or sediment in alkalic condition (Husaini, 2002 ). In nature, there are two types of bentonite, namely natrium and calcium bentonites. The former has relatively higher swelling character which has been used as drilling mud; while the later has non swelling character and utilized as bleaching earth, such as applied for purification of palm oil.

In nature bentonite was also found in various qualities depends on types and quantities of its impurities such as iron and alkali elements. Generally, natural bentonite needs to be beneficiated to obtain a better quality as required by industry. For support catalyst hydrocarbon cracking, the alkali content should be less than 1 %. A method to obtain alkali-free bentonite (alkali and soil alkali) can be carried out by dealcalization. The best dealcalization for clay employes solvents in base and weak acid condition. (Aziz and Saleh, 2005). The solubility of alkali elements of clay mineral depends upon many factors such as particle size, solvent concentration, contact time, percent solid and contact temperature (Aziz, 1987). Therefore, the quality of bentonite can be increased through reduction of impurities in natural bentonite by optimizing those parameters.

In Indonesia bentonite is spread in Sumatra, Java, Kalimantan and celebes with total deposits estimated more than 300 million tonnes. It mostly consists of calcium bentonite (Suhala, 1997). Some sites are already and being exploited in West Java including Karangnunggal, Tasikmalaya, Leuwiliang, Bogor and southern Cianjur.

To improve natural bentonite quality from southern Cianjur, it is necessary to conduct a research of reducing elements of alkali and soil alkali using ammonium hydroxide and citric acid by considering that these two reagents are base and weak acid.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Raw material (bentonite) used in the experiment was derived from southern Cianjur, West Java. Preparation procedure included boulder crushing, grinding, blending to fine size and sieving until obtaining the desired sizes of -150+200 mesh, -200+325 mesh and -325 mesh. Preparation was followed by sampling for characterization. Chemical reagents used were dealcalization reagents, i.e ammonium hydroxide and citric acid.

### 2.2 Methods

Dealcalization of bentonite using ammonium hydroxide and citric acid was done with variation of particle size, solvent concentration, percent solid, time and contact temperature.

## 3. RESULTS AND DISCUSSION

### 3.1 Raw Material Characterization

The chemical composition of bentonite used in this experiment, and the result of x-ray diffraction are shown in Table 1 and Figure 2. From Table 1, it is shown that bentonite consists mainly of $SiO_2$ and $Al_2O_3$, (60.10 % and 16.47 %). While other elements, $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$ and $TiO_2$ are of 8.24%, 0.88%, 0.79%, 1.04% and 0.67% respectively. The high contents of $SiO_2$ and $Al_2O_3$ indicates that the bentonite belongs to alumina-silicate minerals group. From the x-ray diffraction analysis, the sample consists essentially of montmorilonite together with quartz and albite.

### 3.2 Dealcalization by Ammonium Hydroxide

Bentonite dealcalization of using ammonium hydroxide was performed with variation of particle sizes, concentration, solid percentages, time and contact temperatures. The method was applied by measuring Na contents for alkali mineral and Ca contents for soluble soil alkali.

#### 3.2.1 Particle Size Effect

Results of bentonite dealcalization using ammonium hydroxide with different particle size are shown in Figure 3. From Figure 3, it is obvious

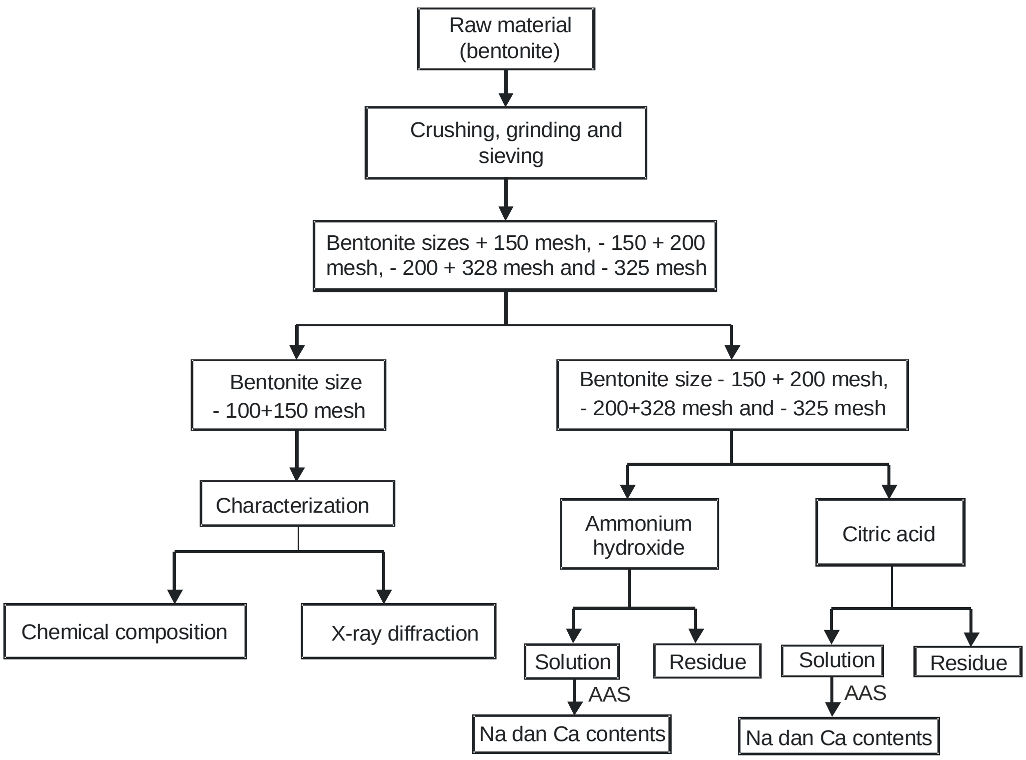


**Figure 1. Flow chart of dealcalization process**

**Table 1. Chemical composition of bentonite**

| Chemical composition (%) | | | | | | | |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ | $TiO_2$ |
| 60.1 | 16.47 | 8.24 | 0.88 | 0.79 | 0.38 | 1.04 | 0.67 |

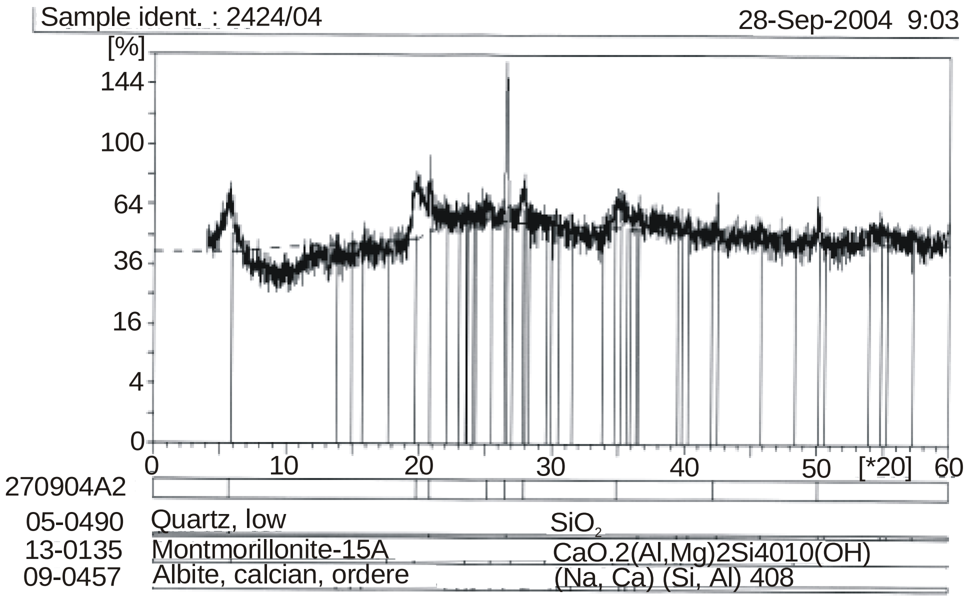


**Figure 2. X-ray diffraction of bentonite**

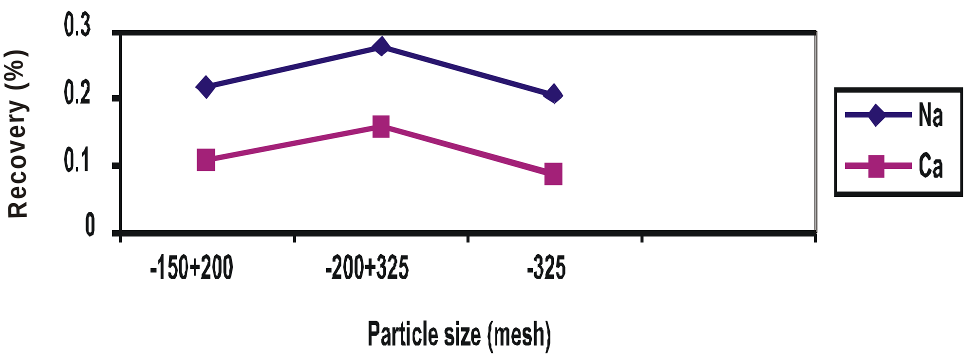


**Figure 3. Recovery of Na and Ca with different particle size**

that the recoveries of Na and Ca increased as the particle size decreased from -150+200 to -200+325 mesh; those were 0.22 % to 0.28 % for Na and 0.11 % to 0.16 % for Ca. It is likely that finer particle size gave larger surface area causing more contact with ammonium hydroxide that allowed more Na and Ca to be dissolved. However, the recovery of Na and Ca decreased as the particle size became finer (-325 mesh) with the value of 0.21% for Na and 0.09% for Ca. Further reduction of particle sizes tends to cover bentonite porous surface. This condition prevent Na and Ca from contacting with ammonium hydroxide thus reducing dissolution of Na and Ca.

### 3.2.2 Ammonium Hydroxide Concentration Effect

Recovery of Na and Ca from dealcalization of bentonite using ammonium hydroxide at different concentration is shown in Figure 4. It is shown that the recovery of Na and Ca from dealcalization bentonite increased as the concentration of ammonium hydroxide increased from 1 N to 4 N; those were 0.28% to 0.42% for Na and 0.05% to 0.21% for Ca. However, the Na and Ca recovery decreased at higher ammonium hydroxide concentration of 6 N with recovery 0.36% of Na and 0.11% of Ca. This is due to the exessive of ammonium hydroxide concentration made the solution into basic condition so the Na and Ca could not be dissolved but deposited.

### 3.2.3 Percent Solid Effect

Results of Na and Ca recovery from dealcalization of bentonite using ammonium hydroxide at different percent solid are shown in Figure 5. Figure 5 shows that Na and Ca recovery from dealcalization bentonite increased from 1.35% to 1.52% for Na and from 0.61% to 0.73% for Ca by increasing percent solid 5% to 10%. However, Na and Ca recovery decreased again at percent solid of 15%.

### 3.2.4 Contact Time Effect

Results of Na and Ca recovery from bentonite dealcalization using ammonium hydroxide at different contact time are shown in Figure 6. Figure 6 shows that recovery of Na from bentonite dealcalization increased from 1.46 % at contact time of 12 hours to 11.29 % at contact time of 36 hours. Similar results were obtained from 0.76 to 9.59 % for Ca. While at longer contact time than 36 hours, recovery of Na and Ca decreased become 4.85 % for Na and 4.29 % for Ca due to evaporation of ammonium hydroxide and deposition of Na and Ca by the solvent as a consequence of reaction equilibrium shifted to the right.

### 3.2.5 Contact Temperature Effect

The results of Na and Ca recovery from dealcalization of bentonite using ammonium hydroxide at different contact temperature are given in Figure 7. As expected, when temperature increased from 27 to 100$^{o}$ C, the Na-Ca recovery also increased (5.03 to 32.55 % for Na; 6.19 to 29.14 % for Ca). Nevertheless, the recovery decreased again at temperature of 135$^{o}$ C because of ammonium hydroxide evaporation.

## 3.3 Dealcalization Using Citric Acid

Bentonite dealcalization using citric acid was done in analogous way with those of ammonium hydroxide through variations of particle size, citric acid concentration, percent solid, time and temperature by measuring Na and Ca contents.

### 3.3.1 Particle Size Effect

The results of Na and Ca recovery from dealcalization of bentonite using citric acid at different particle size are shown in Figure 8. In Figure 8, it can be seen that Na and Ca reco very increased in accordance with the decrease of particle size from 3.26 % of Na and 0.39 % of Ca at particle sizes of -150+200 mesh to 4.15 % of Na and 0.51 % of Ca at particle size of -325 mesh. Finer particle sizes generated larger surface area which permit more contact between citric acid and Na and Ca, thus resulted in more solubility of Na and Ca.

### 3.3.2 Concentration Effect

Results of Na and Ca recovery from dealcalization of bentonite using citric acid at different concentration of citric acid are shown in Figure 9. Figure 9 shows increased recovery of Na and Ca at increased citric acid concentration from 1 N to 2 N (4.11 to 4.41 for Na and 0.51 to 1.26 % for Ca). Na and Ca recovery started to decrease at concentration of 4 N become 3.72% for Na and 0.89% for Ca.

### 3.3.3 Percent Solid Effect

Results of Na and Ca recovery from dealcalization

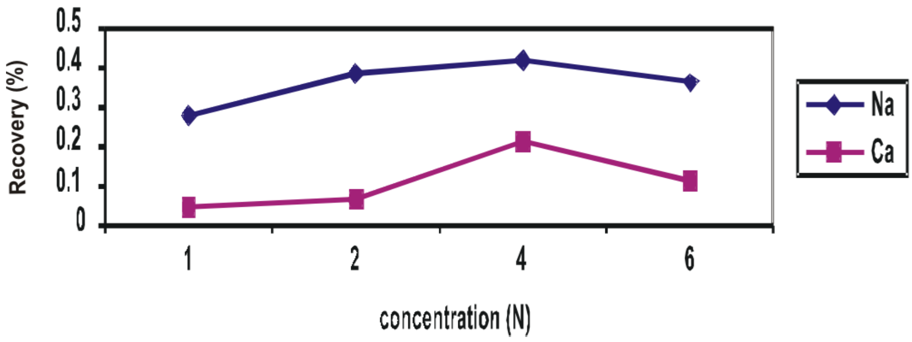


**Figure 4. Graph of recovery Na and Ca at different concentration**

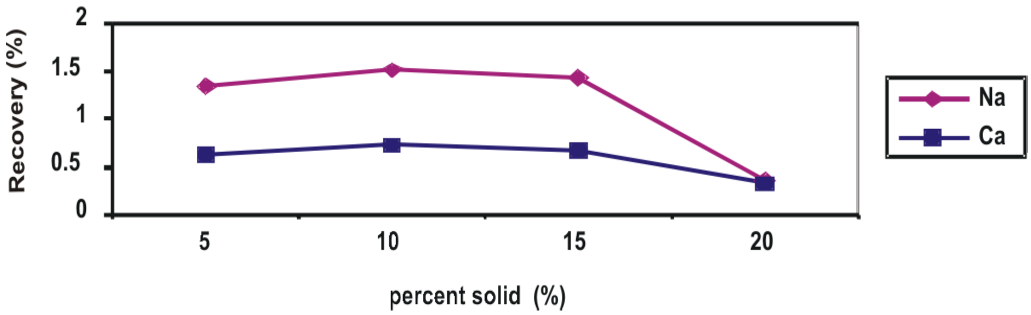


**Figure 5. Graph of Na and Ca recovery at different percent solid**

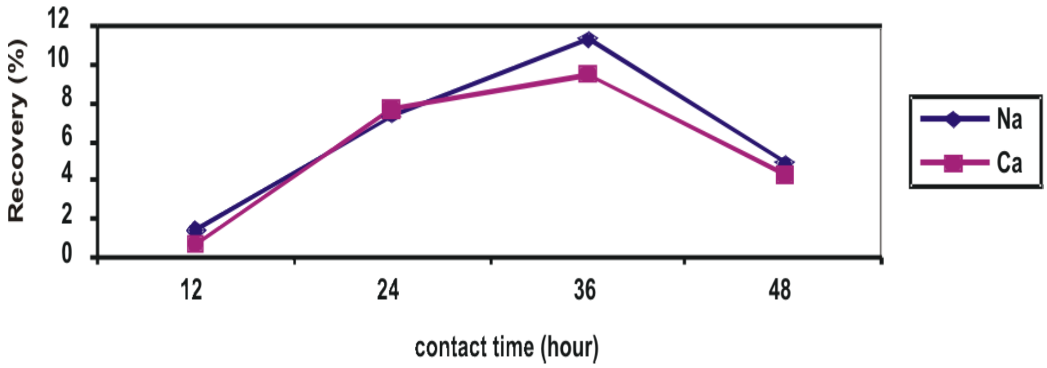


**Figure 6. Graph of Na and Ca recovery at different contact time**

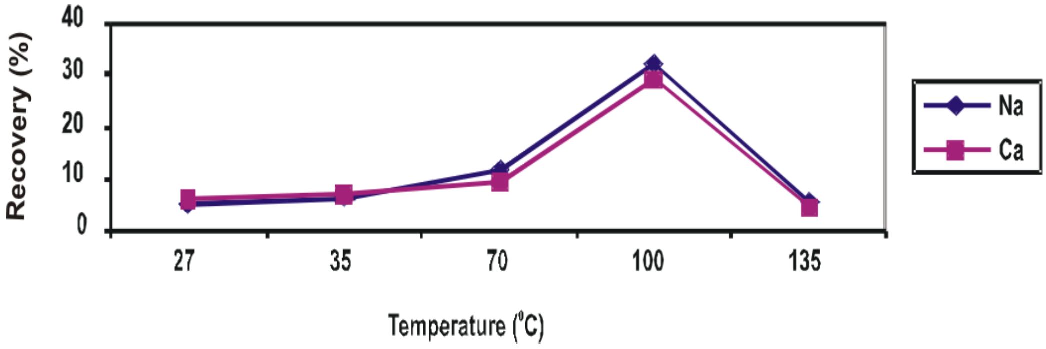


**Figure 7. Graph of Na and Ca recovery at different contact temperature**

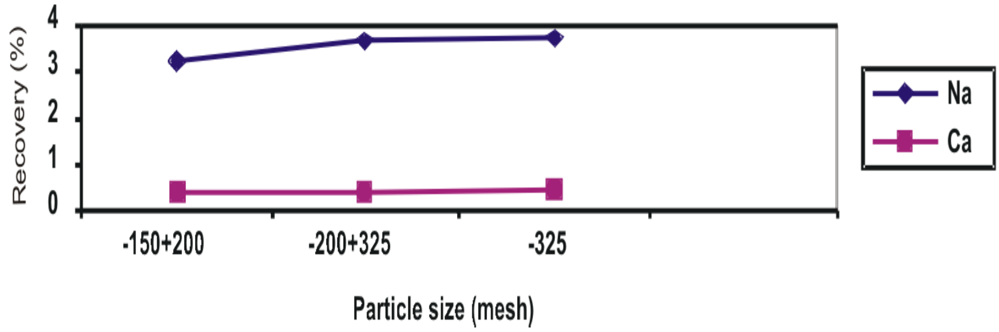


**Figure 8. Recovery of Na and Ca at different particle size**

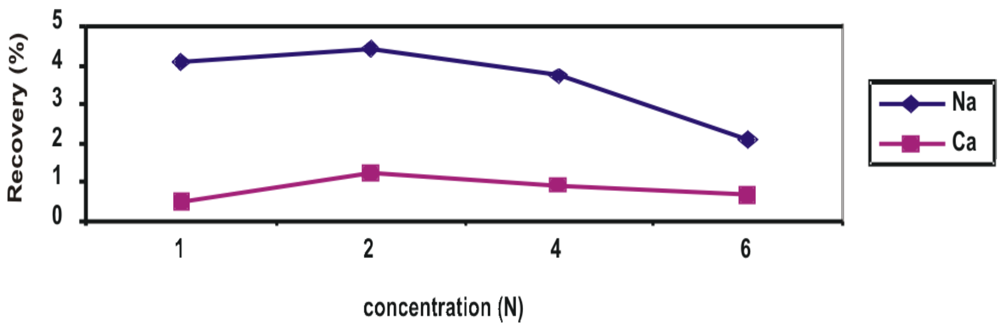


**Figure 9. Na and Ca recovery at different citric acid concentration**

of bentonite using citric acid at different percent solid are shown in Figure 10. Figure 10 demonstrates that the recovery of Na and Ca along together with the increase of percent solid from 5 to 10 (2.13 to 4.82% for Na and 0.42 to 2.12% for Ca). The decrease of Na-Ca recovery started at 15 % percent solid became 2.48% for Na and 1.29% for Ca. Achievements of greater recovery of Na and Ca at low percent solid or at liquid mixture condition causing more movements of solvent ions in approaching the alkali elements in bentonite; thus resulted in increased solubility of the solvent to dissolve Na and Ca. While at solid mixture condition or high percent solid resulted in slow and few movements of solvent ions in approaching Na and Ca thus causing the alkalis less dissolved in bentonite.

### 3.3.4 Contact Time Effect

The results of Na and Ca recovery from dealcalization of bentonite using citric acid at different contact time are shown in Figure 11. Figure 11 illustrates that Na and Ca recoveries increased by increasing contact time from 12 hours to 24 hours (4.69 to 12.95% for Na and 1.99 to 11.55% for Ca). While above 24 hours the recovery decreased to 10.71 for Na and 8.59% for Ca.

### 3.3.5 Variation of Contact Temperature

Results of Na and Ca recovery from dealcalization of bentonite using citric acid at different contact temperature are shown in Figure 12. Figure 12 illustrate that the recovery of Na and Ca in dealcalization of bentonite increased from temperature of 27 to 100$^{o}$C (8.09 to 33.01% for Na and 9.16 to 30.07% for Ca). Above 100$^{o}$C, the Na and Ca recovery decreased to 14.41% for Na and 7.49% for Ca because such higher temperature resulted in much faster reaction which causing the reaction shifted toward reactant.

## 4. CONCLUSIONS

Dealcalization using ammonium hydroxide shows the recovery of Na (32.55 %) and of Ca 29.14 % at particle size of -200+325 mesh, concentration of 4 N, 10% percent solid, contact time of 36 hours and temperature of 100$^{o}$C. While dealcalization using citric acid, the optimum condition was at

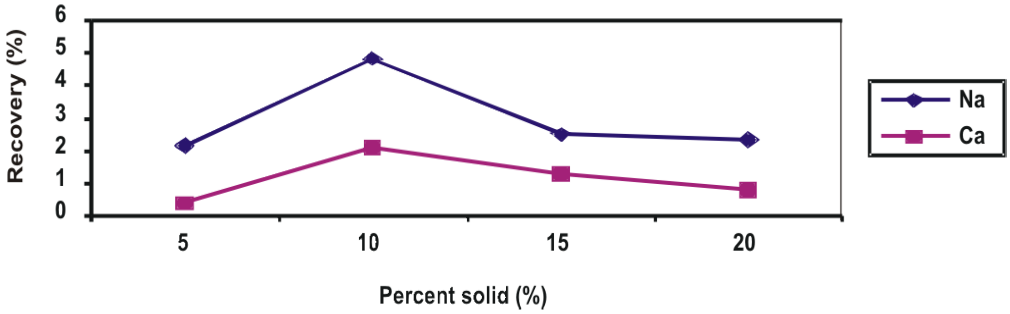


**Figure 10. Recovery of Na and Ca at different percent solid**

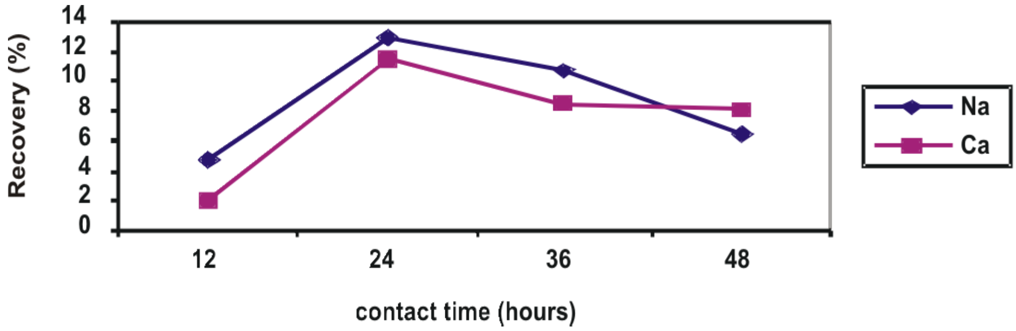


**Figure 11. Na and Ca recovery at different contact time**

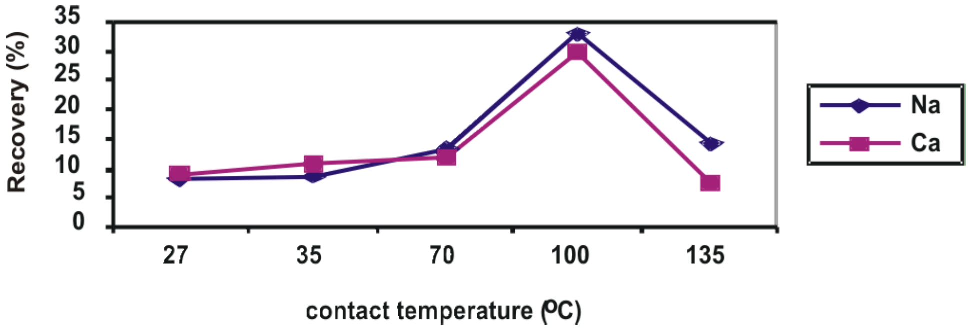


**Figure 12. Na and Ca recoveries at different contact temperature**

particle size of -325 mesh, concentration of 2N, percent solid of 10%, contact time of 24 hours, temperature of 100°C with recovery as much as 33.01% for Na and 30.07% for Ca. Results also show that both solutions gave better recovery for Na rather than for Ca. Yet, experiments using citric acid was better than that of using ammonium hydroxide as revealed from higher recovery of alkali elements.

The results of Dealcalization using ammonium hydroxide and citric acid in this work has not met standard of bentonite specification required by industry especially as supportive catalyst for hydrocarbon cracking. It only extracted approximately 30 percent of alkaline.

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