Research Article

Preparation and Characterization of Acids and Alkali Treated Kaolin Clay

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Abstract

Kaolin was refluxed with HNO_3, HCl, H_3PO_4, CH_3COOH, and $NaOH$ of 3 M concentration at 110 °C for 4 hours followed by calcination at 550 °C for 2 hours. The physico-chemical characteristics of resulted leached clay were studied by X-Ray Fluorescence spectroscopy (XRF), X-Ray Diffraction (XRD), Fourier Transformed Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA), Scanning Electron Microscope (SEM), Temperature Programmed Desorption (TPD) ammonia method, and N_2 adsorption techniques. XRF and FTIR study indicate that acid treatment under reflux conditions lead to the removal of the octahedral Al^{3+} cations along with other impurities. XRD of acid treated clay shows that, the peak intensity was found to decrease. Extent of leaching of Al^{3+} ions is different for different acid/base treatment. The chemical treatment increased the Si/Al ratio, surface area and pore volume of the clay. Thus, the treated kaolin clay can be used as promising adsorbent and catalyst supports. © 2013 BCREC UNDIP. All rights reserved

Keywords: Kaolin; acid/base treatment; physico-chemical characteristics; adsorbent; catalyst

1. Introduction

Physical and chemical behaviors of clay minerals have been studied by numerous researchers due to their adsorbing and catalytic properties. This behavior is governed by the extent and nature of their external surface which can be modified by suitable treatment techniques. There are broadly two different treatments or modification methods of clay minerals studied by different researchers such as (1) physical modification (thermal or microwave treatment) which involves alteration of chemical composition and crystalline structure by the effect of high temperature, (2) chemical modification (by acids, bases, organic compounds) which is usually by the alteration of structure, surface functional groups and surface area [1].

The most common physical modification is thermal treatment which involves the alteration of chemical composition and/or crystalline structure by the effect of temperature. The structure and composition of clay minerals can be modified by

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heating at high temperature [2]. Some physico-chemical properties such as swelling, strength, cation exchange capacity, particle size, specific surface area, surface acidity and catalytic activity as well as mineralogy can change considerably on the thermal treatment [3, 4]. In addition to thermal treatment, microwave heat treatment also plays an important role for modification of clay materials [5]. Clark et al. has reported that the temperature and time required by microwave heating method for preparing adsorbents are far shorter than by the conventional thermal activation method and this method is simple, economic, time saving and energy efficient [6].

Acid treatment is one of the most common chemical treatments for clay minerals and has been used to increase the specific surface area and the number of acidic centers, modify the surface functional group and to obtain solids with high porosity. Numerous studies have been reported on the acid treatment of clays, especially on bentonite-smectite or montmorillonite, vermiculite, kaolin, palygorskite-sepiolite and glauconite [7-15]. The various types of acids used for acid treatment including inorganic acids such as hydrochloric, sulfuric, nitric and organic acids such as acetic, citric, oxalic and lactic. Among all of these, hydrochloric acid and sulfuric acid are probably the most widely used in acid activation, because it shows strong affection by the process parameters and superior results in specific surface area, porosity and adsorption capacity [16].

Hussin et al. has performed the basic treatment of clay and reported that the active centers increases and surface area decreases with NaOH treatment and cost of sodium hydroxide is much lesser than that of inorganic acids such as H_2SO_4 and HCl. However, the base treated clay materials are suitable only for some applications [1].

Several problems such as corrosion of the process vessels, increasing of free fatty acids, peroxide value in oil products and other environmental problems occur when acid treated clay is used. This led to modification of clay with cationic and anionic surfactants [Cetyl trimethyl ammonium bromide and linear alkyl benzene sulfonate] for the removal color pigment, free fatty acids and peroxide value [17]. Intercalation or pillaring is also a clay treatment method that alters the properties of bleaching earth by using combination of chemical and physical treatments in which a layered compound is transformed in a thermally stable micro and/or mesoporous material with retention of the layer structure. Pillared clay minerals have magnetized much attention from the industry due to their microporous nature and catalytic potential [18, 19].

Recently, we have carried out the acid activation of kaolin with sulphuric acid of different concentrations under refluxed condition followed by a systematic analysis of the treated kaolin samples with wide characterization techniques to understand the changes in physico-chemical properties. It has been concluded that sulphuric acid treatment at and above 5M concentration almost destroys the crystalline structure and other properties to a considerable extent [12]. Studies on different acids and alkaline treatment of kaolin with a complete characterization and comparison of results have not been studied. Therefore, in the present work, kaolin is treated with different other acids such as HNO_3, HCl, H_3PO_4, CH_3COOH, and base NaOH of 3 M concentration to compare their effects on modifications in physico-chemical properties of kaolin after treatment with different reagents.

2. Experimental Works

2.1. Materials

The kaolin used in this experiment was procured commercially from Chemtex Corporation, Kolkata, India. The sample was used as such without any further modification for the acid and alkali treatment. The chemical composition of the sample is as follows: SiO_2 = 43.12%, Al_2O_3 = 46.07%, Fe_2O_3 = nil, MgO = 0.027%, CaO = 0.030%, ZnO = 0.0064%, K_2O = 0.01%, TiO_2 = 0.74% and loss on ignition = 9.9%. From the proximate analysis and XRD report it could be concluded that the major component of the clay is kaolinite with Hinckley index of 0.4. Some traces of impurities (may be mica, quartz and feldspar which could not be traced in the XRD report) are also present which contribute the components other than SiO_2 and Al_2O_3 [12].

2.2. Acid Activation

The thermo-chemical activation was carried out by adding 50 g of the clay to 500 ml of solution of different acids and a base of 3 M concentration and refluxing at 110 °C under the atmospheric pressure in a round bottomed flask equipped with a reflux condenser for four hours. The resulting clay suspension was then rapidly quenched by adding 500 ml ice cold water. The content was then filtered, repeatedly washed with distilled water to remove any unspent reagent, dried in an oven, calcined at 550 °C for two hours and ground in a mortar pastel to powder form. The untreated sample is referred to as K and treated samples are referred to as $KHNO_3$, KHCl, KH_3PO_4, KCH_3COOH, and KNaOH in the subsequent text where the name refers to the treated kaolin with different acid and base as indicated.

2.3. Characterization Techniques

The treated kaolin clay materials were characterized by X-Ray Fluorescence spectroscopy (XRF), X-Ray Diffraction (XRD), Fourier Transformed Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA), Scanning Electron Microscopy (SEM), Temperature Programmed Desorption (TPD) ammonia method, and by sorptiometric studies. The XRF analysis of the samples were done by using a Model-PW2400 of Phillips with X-ray tube of rhodium anode and scintillation detector with a current 40 mA and voltage 40 mV. The X-ray diffraction data was collected using a Philips Analytical X-ray Instrument, X'Pert-MPD (PW 3020 vertical goniometer and PW 3710 MPD control unit) employing Bragg–Brentano para focusing optics. The XRD patterns were recorded in the range 2θ of 10–70° with a scanning rate of 2 °/min. The FTIR spectra were recorded on a Perkin-Elmer infrared spectrophotometer as KBr pellets with resolution of 4 cm-1, in the range of 400-4000 cm-1. The sample and analytical grade KBr were dried at 100 °C overnight prior to the FTIR analysis. The Thermogravimetric analysis were carried out by a SHIMADZU DTG-60/60H instrument. A known weight of the sample was heated in a silica crucible at a constant heating rate of 10 °C/min operating in a stream of N_2 atmosphere with a flow rate of 40 ml/min from 35 - 600 °C. Nitrogen adsorption–desorption measurements (BET method) were performed at liquid nitrogen temperature (−196 °C) with an Autosorb BET apparatus from Quantachrome Corporation. The BET analysis procedure is automated and operates with the static volumetric technique. Before each measurement, the samples were outgassed first at 200 °C for 2 hours, at 5×10^{-3} torr and then at room temperature for 2 hours, at 0.75×10^{-6} torr. The isotherms were used to determine the specific surface areas using the BET equation. The Scanning Electron Micrographs were taken on a JEOL-JSM 5600 LV microscope, equipped with a 6587 EDS (energy dispersive X-ray spectrometry) detector, using an accelerating voltage of 15 kV. The samples were deposited on a sample holder with an adhesive carbon foil and sputtered with gold. The acidic properties of the catalysts were probed by ammonia TPD measurements in Micromeritics 2900 TPD equipment. Previously, the samples were outgassed under He flow (50 Nml/min) by heating with a rate of 15 °C/min up to 560 °C and remaining at this temperature for 30 min. After cooling to 180 °C, the samples were treated with a 30 Nml/min ammonia flow for 30 min. The physisorbed ammonia was removed by passing a He flow at 180 °C for 90 min. The chemically adsorbed ammonia was determined by increasing the temperature up to 550 °C with a heating rate of 15 °C/min, remaining at this temperature for 30 min, and monitoring the ammonia concentration in the effluent He stream with a thermal conductivity detector.

3. Results and Discussion

3.1. XRF Characterization

The XRF analysis was carried out to know the chemical compositions of the clay and the subsequent chemical changes that occurred due to treatment. Table 1 shows the results of chemical analysis of the parent and treated kaolin. The parent clay contains alumina and silica which are in major quantities where as other oxides such as magnesium oxide, calcium oxide, potassium oxide, zinc oxide and titanium oxide are present in trace amounts.

After the acid treatment, it was observed that the composition of the kaolin changes considerably. The Al_2O_3, MgO, CaO, and K_2O contents decreases and SiO_2 content increased in the treated kaolin progressively on treatment with different reagents (acids and base). The decrease in the alumina content in the treated sample can be ascribed to the leaching of the Al^{3+} ions from the octahedral layer due to hydrolysis under acidic/alkaline conditions.

During treatment, it was observed that the concentration of CaO, MgO, K_2O, TiO_2 and V_2O_5 reduced, but that of ZnO remained almost unchanged with any types of reagent. The extent of leaching depends on the type of reagent and is in the order $NaOH = HNO_3 > HCl > H_3PO_4 > CH_3COOH$. For example, with 3 M NaOH and HNO_3 treatment, the Al_2O_3 content decreases from 46.07 to 29.30% and 27.88% respectively, where as the SiO_2 content increases from 43.12 to 56.14% and 56.42% respectively. Thus the Si/Al ratio of the kaolin treated with different reagent increases in the same trend. The XRF study clearly indicates that leaching occurred in a sequential manner due to attack at tetrahedral layer resulting in the dealumination of clay. This can be interpreted due to the increasing strength and leaching ability of the respective reagents.

3.2. XRD Characterization

The structural changes that occurred in the clay material after the acid or alkali treatment were studied using X-ray diffraction technique. Figure 1 shows the XRD profiles of the untreated and treated kaolin samples. The parent clay shows well defined reflections at 2θ value of 12⁰, 25⁰ (corresponding to the *d* values of 7.154 Å. These peaks correspond to the reflections from [001],

Table 1. XRF analysis of different kaolin

Material	Chemical content (% weight)								
	SiO₂	Al₂O₃	MgO	CaO	K₂O	ZnO	TiO₂	V₂O₅	Si/Al
Kaolin	43.12	46.07	0.027	0.030	0.010	0.0064	0.74	0.003	0.82
KCH3COOH	44.03	43.81	0.026	0.017	0.01	0.0062	0.40	0.003	0.885
KH3PO4	45.83	41.51	Nil	0.018	0.007	0.0064	0.34	0.003	0.972
KHCl	48.80	37.61	0.016	0.017	0.01	0.0064	0.26	0.001	1.144
KHNO3	56.42	27.88	0.02	0.008	0.008	0.0064	0.23	0.002	1.782
KNaOH	56.14	29.30	0.030	0.186	0.017	0.0064	0.12	Nil	1.688

which are typical characteristic peaks of kaolinite. After acid treatment, the peak intensity of the clay was found to decrease and extent of decrease follows the trend $HNO_3 > HCl > H_3PO_4 > CH_3COOH$, since leaching is quite severe with strong acids. This is attributed to the structural disorder that occurred owing to the acid leaching, which affects the crystalline character of the clay. With NaOH treatment the peak intensity increases and narrowed. The increase in intensity and/or narrowing of the peak may be related to the increase of crystallite size and/or the decrease of the mean lattice strain [20].

3.3. FTIR Characterization

The FTIR spectrums of kaolin and treated kaolins are shown in Figure 2 and the corresponding band assignments are shown in Table 2. In the O-H stretching region, the parent and acid treated clay shows three prominent bands at 3620, 3653 and 3695 cm⁻¹ corresponds to Al-OH stretching. Inner hydroxyl groups, lying between the tetrahedral and octahedral sheets give the absorption at 3620cm⁻¹. A strong band at 3695 cm⁻¹ is related to the in phase symmetric stretching and a weak absorption at 3653 cm⁻¹ is assigned to out-of-plane stretching vibrations. The band observed at 3445 cm⁻¹, assigned to the high amount of water physisorbed on the surface of the clay [21, 22]. There was not much variation in the peak pattern for 3 M H_3PO_4 and CH_3COOH acid treated kaolin. However with HNO_3 and HCl treatment the peak intensity was found to decrease progressively indicating penetration of protons into the clay mineral layers and attack to the structural hydroxyl groups resulted in the dehydroxylation and a successive leaching of the Al ions from the octahedral layer [5]. For the NaOH treated kaolin the structural hydroxyl vibration band is extremely weak.

In the bending region mode, the clay materials show a series of IR bands with peak maxima at 1634, 914, 795 and 755 cm⁻¹. The peak at 1634 cm⁻¹ is quite intense is attributed to the bending vibration mode of physisorbed water on the surface of
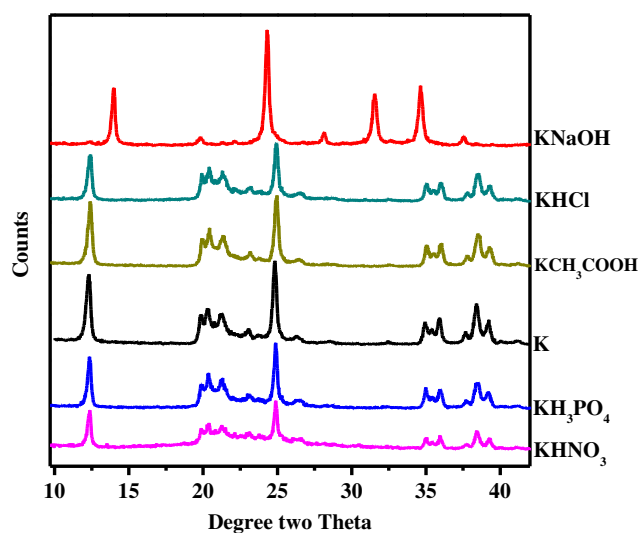

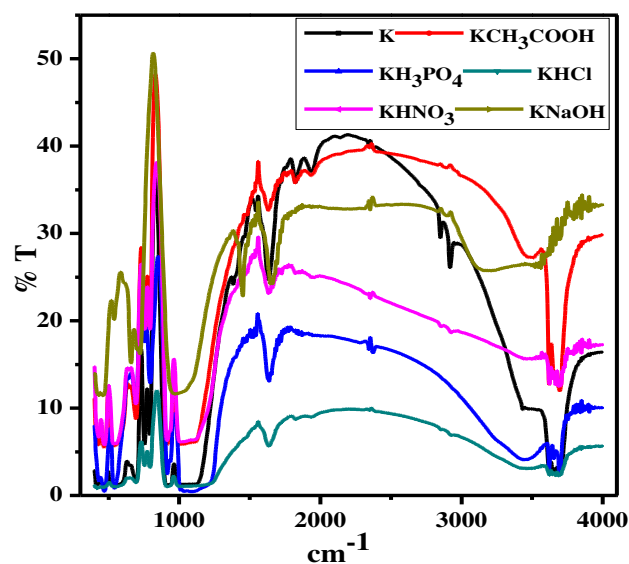**Figure 1**. XRD results of different kaolin

Figure 2. FTIR results of different kaolin

free silica produced due to leaching [22]. This peak was found to be absent in case of the HNO₃ treated clay due to structural disintegration. The IR peaks at 914, 795 and 755 cm⁻¹ can be assigned to the Al–Al–OH, Al–Mg–OH and Si-O-Al vibration of the clay sheet. The high intense 914 cm⁻¹ peak due to vibrations of inner OH groups was found to be drastically reduced for HCl and HNO₃ treated clay. It can be concluded that, when the acid strength is more the de-alumination process is facilitated rapidly, during acid treatment [23].

Again well resolved strong bands in the 1120-1000 cm⁻¹ region is due to Si-O stretching in untreated kaolinite which changed in shape and position due to structural changes in the tetrahedral cations. In addition, a new peak was observed at 805 cm⁻¹ for the acid treated sample, which gained intensity with increase in the acid strength [21, 23]. This peak is due to the formation of free amorphous silica. The FTIR result is in clear agreement with the XRF and XRD studies which indicates sequential degradation of the clay sheet upon acid treatment. The FTIR of KNaOH showed wide water bands centered at about 3420 and 1655 cm⁻¹,the asymmetric stretching of the tetrahedral units at 985 cm⁻¹ with a shoulder at 1020 cm⁻¹, the symmetric stretching at 665 cm⁻¹, and the bending at 478 cm⁻¹. Moreover, the presence of carbonate groups was clearly shown by a wide band centered at 1440 cm⁻¹.

3.4. TG-DTA Analysis

The TGA curves (Figure 3a) of the pure and treated kaolin show two well-defined weight loss regions due to the loss of physisorbed water (below 200 °C) and dehydroxylation of coordinated and structural water (above 450 °C). In general, clay materials contain three kinds of water molecules in their structure. The physisorbed and interlayer water is loosely bound and are mobile they can be removed by heat treatment below 200 °C. The water molecules present in the first coordination sphere of the interlayer ions are strongly bonded and they require higher temperature in the range of 300-500 °C for their removal. Finally, the structural hydroxyl groups can condense and dehydrate in the temperature range of 500-800 °C. In the present study, the low temperature weight loss can be assigned to the physisorbed water, where as the high temperature weight loss is due to the dehydration and dehydroxylation of the clay sheet. Comparing the TGA profile of the parent and the acid treated clay it was observed that acid treatment increased the amount of physisorbed water and it increased with increased strength of the acid (HNO₃ > HCl >H₃PO₄ > CH₃COOH). It is extraordinarily high in case of sodium hydroxide treated kaolin. This may be due to the fact that chemical treatment increased the amount of amorphous silica and also the surface area which made the water adsorption higher. However, in the high temperature weight loss regions, the percentage loss is low for treated clay as compared to the parent clay due to the removal of octahedral Al ions along with the concurrent removal of structural hydroxyl groups after acid treatment.

The DTA profiles of the clay and acid treated clay are shown in Figure 3b supports the weight loss pattern due to water removal in the TGA study. The DTA curve of untreated kaolin showed two endothermic peaks at 56 and 531 °C. The endothermic peak centered at around 56 °C may be due to physisorbed water and a large peak at 531 °C might be due to the liberation of water caused by dehydroxylation of co-ordinated and structural water molecules. Increase in acid strength due to change in type of acid increased the physisorbed water and decreased the structural and coordinated water leading to change in the endothermic

Table 2. Important IR assignments of different kaolin

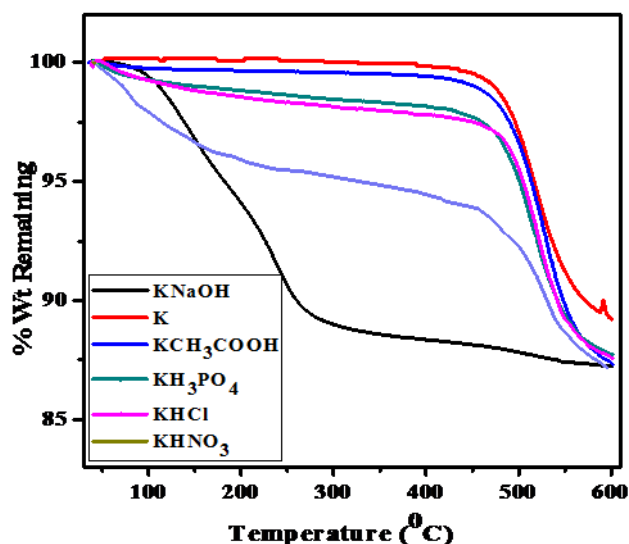| Band (cm⁻¹)	Peak Assignments
3445	Al--O-Hstr (physisorbed and interlayer water)
3620, 3653 & 3695	Al--O-Hstr (structural hydroxyl groups, octahedral
1634	H-O-Hbending(physisorbed)
912	Al–Al–OHstr,
1032, 1101 & 1114	Si-Ostr
795	Al–Mg–OHstr
755	Si-O-Alstr
805	Si-Ostr
693	Si-Ostr, Si-O-Alstr
541	Si-Ostr, Si-O-Alstr
472	Si-Ostr

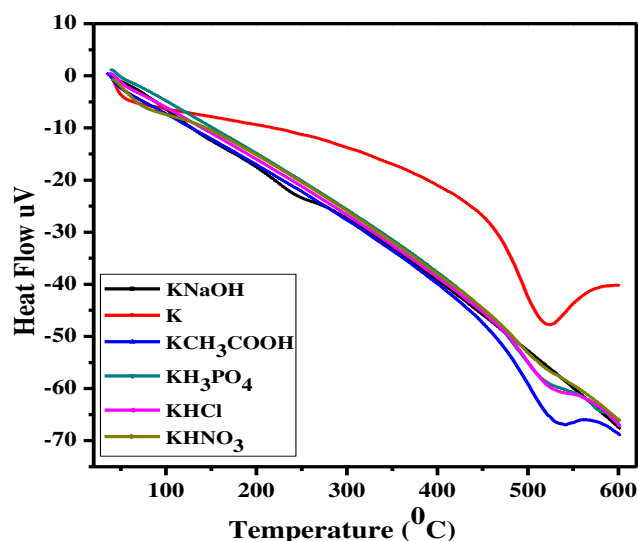**Figure 3a**. TGA of different kaolin

Figure 3b. DTA of different kaolin

peaks in treated samples. The thermal analyses of the alkaline treated sample showed completely different curve as compared to acid treated kaolin samples. Thus, the weight loss is very high at low temperature, between room temperature and 250 °C. It may be considered that the fixed carbonate anions contributed in a small amount to the weight loss at high temperature.

3.5. BET Surface Area and Pore Volume

The surface area and pore volume of the pure and treated kaolin obtained using N_2 adsorption-desorption isotherms summarized in Table 3. The pore volume and BET surface area increased with increasing acid strength. Alkali treatment also increased the surface area and pore volume. This can be explained due to occurrence of the de-alumination process and thus surface disintegration.

The increase in pore volume due to acid treatment is more prominent as compared to alkali treatment. Production of finely dispersed Si oxides

Table 3. BET surface area and pore volume of different kaolin

Material	Surface Area (m²/g)	Pore Volume (cc/g)
Kaolin	23	0.361
KCH_3COOH	38	0.504
KH_3PO_4	42	0.658
KHCl	78	1.083
$KHNO_3$	86	1.124
KNaOH	76	0.591

from destruction and leaching of kaolin, by removal of different cations plugging the surface pores or interlamellar spaces, by formation of surface pores and cracks as well as by decrease in mineral size leading to increased pore volume due to acid treatment. Under alkaline treatment, similar processes may occur together with an accumulation of hydroxides of Mg and Ca [24].
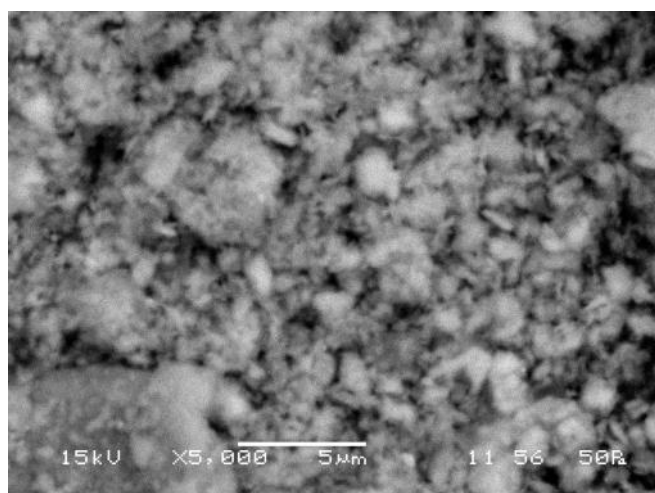
3.6. SEM Analysis

The scanning electron micrographs of the different kaolin clay samples are presented in Figures 4(a-f) which shows the morphological features. The SEM micrograph of KC reveals the presence of large particles that appeared to have been formed by several flaky particles stacked together in form of agglomerates. The SEM images of treated kaolin show different particles morphology. The micrographs of KCH_3COOH and KH_3PO_4 indicate the disaggregation and decrease in size of clay structure on acid treatment and that of KHCl, $KHNO_3$ and KNaOH shows well-bonded aggregates rather than detached particles.
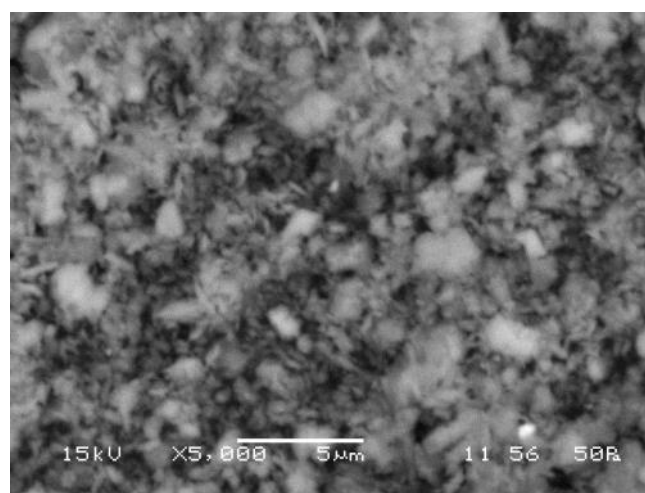
3.7. Acidity of Kaolin

The acidity of aluminosilicates is characterized in terms of Bronsted and Lewis acid sites. Bronsted acid sites are formed by aluminum atoms connected to silicon by a so-called "bridging hydroxyl" Al–(OH)–Si where the negative charge generated is compensated for by a proton. Lewis acid sites are composed of aluminum with low coordination or $\equiv Si^+$ ions formed from dehydroxylation. Therefore, the acidity of an alumino-silicate is related to its silica and aluminum contents, and in-

(a)

(b)
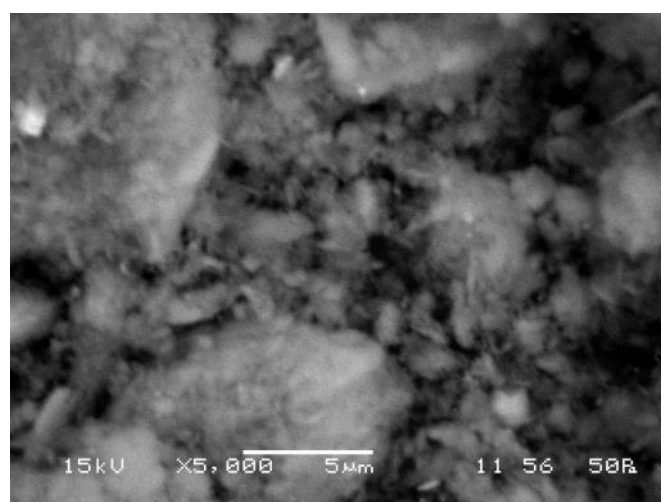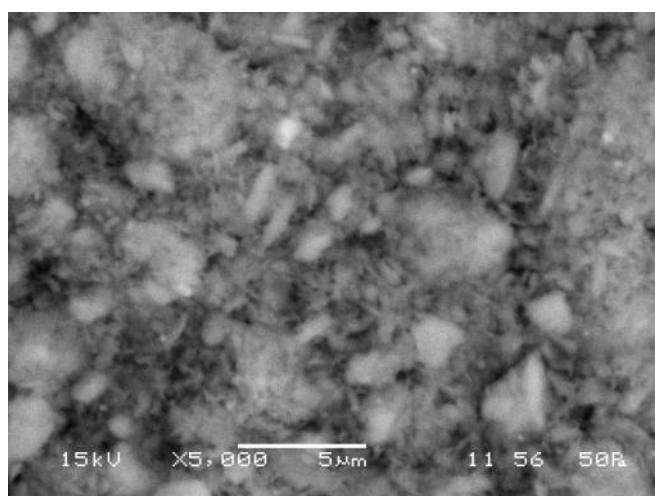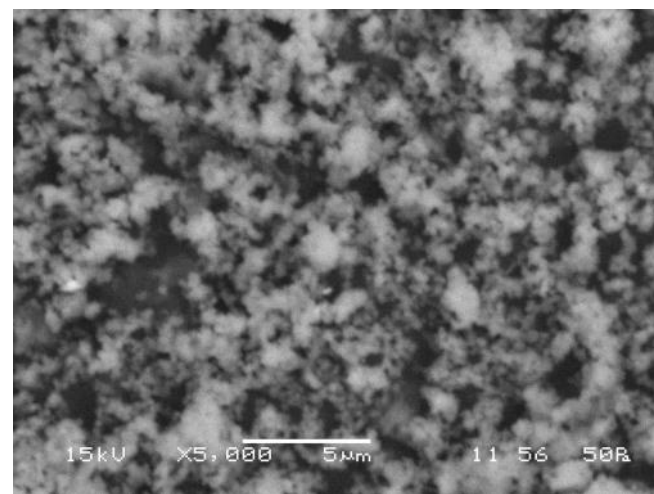

(c)

(d)

(e)

(f)

Figure 4. SEM images of treated kaolin by: (a) Kaolin clay; (b) CH$_3$COOH; (c) H$_3$PO$_4$; (d) HCl; (e) HNO$_3$; (f) NaOH

Table 4. Acidity values of different kaolin

Materials	Acidity (mmol/g)
Kaolin	0.049
KCH_3COOH	0.109
KH_3PO_4	0.114
KHCl	0.225
$KHNO_3$	0.341
KNaOH	0.112

Figure 5. TPD NH_3 plots of different kaolin

creases linearly with increasing silica to aluminum ratio in the sample (Table 1). Acidity values of pure kaolin and acid, alkaline treated kaolin is shown in table 4. Lower acidity of KNaOH can be explained due to the neutralization of acid sites formed due to leaching by the strong alkali NaOH.

Figure 5 shows typical plots of ammonia desorption rates as a function of temperature for samples so treated. It can be seen from TPD plots that desorption of ammonia from all the samples starts at about 200 °C and ammonia desorption plots of samples Kaolin Clay (KC), KCH_3COOH, KH_3PO_4 contain two peaks. In case of the first peak, that occurs at 200-300 °C is assigned to desorption of ammonia from Lewis acid sites as week coordinate bond will break at low temperature. The second weak peaks at around 500-600 °C is due to desorption of Bronsted acid bound (strong ionic bond) ammonia molecules. Similarly, the plots of the ammonia desorption for samples KHCl and $KHNO_3$ contain three peaks out of which first one is due to Lewis acid sites which is at lower temperature and other two at higher temperature may be due to Bronsted acid sites. The lower ammonia desorption rate and as a result the less acidity were found to be on KC, KCH_3COOH, and KH_3PO_4 samples. Due to the low Si/Al-ratio of these kaolinite samples both SiOH and AlOH sites are center responsible for the ammonia adsorption. Slightly high acidity is due to dealumination. Other two samples KHCl and $KHNO_3$ have more acidity due to higher rate of desorption.

4. Conclusion

The effect of the acid and alkaline treatment on the structural and chemical properties of kaolin clay has been studied. The XRF and SEM study indicated clearly the leaching and disintegration of the clay sheet after treatment with different acid and alkali. The Al_2O_3, MgO, CaO, K_2O, TiO_2, and ZnO contents in the treated material decreased progressively simultaneously increasing the SiO_2
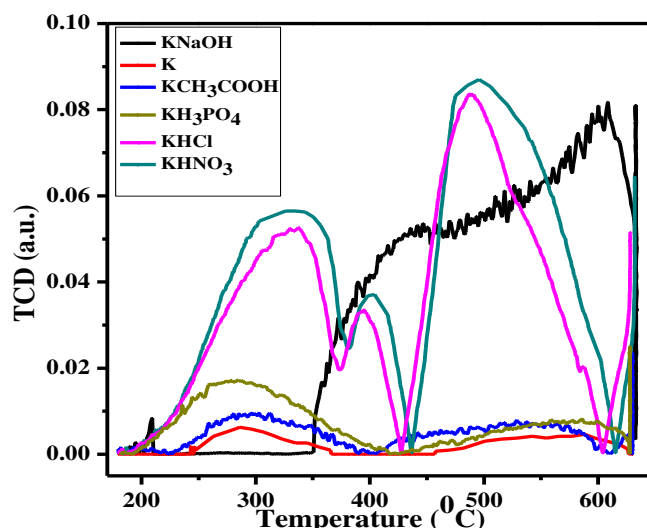
content. XRD studies of the acid treated clay indicated the structural transformation of the clay sheet upon acid treatment. After acid treatment the peak intensity of the clay was found to decrease and extent of decrease follows the trend HNO_3 > HCl > H_3PO_4 > CH_3COOH. FTIR spectrum of the acid treated kaolinite clay shows that there is not much variation in the peak pattern for H_3PO_4 and CH_3COOH acid treated kaolin. The peak intensity is found to decrease progressively for HNO_3 and HCl acid treated kaolin and for NaOH treated kaolin, the structural hydroxyl vibration band is extremely weak. TGA profile of the parent and the acid treated clay shows that acid treatment increased the amount of physisorbed water and it increased with increased strength of the acid (HNO_3 > HCl > H_3PO_4 > CH_3COOH). It is extraordinarily high in case of sodium hydroxide treated kaolin. The DTA profiles of the clay and acid treated clay supports the weight loss pattern due to water removal in the TGA study. The increase in pore volume and BET surface area due to acid treatment is more prominent as compared to alkali treatment. The SEM micrograph of KC reveals the presence of large particles which are aggregated after treatment with HCl, HNO_3, NaOH and disaggregated when treated with H_3PO_4 and CH_3COOH. The acidity was less in case of pure kaolin and after treatment with CH_3COOH and H_3PO_4 acids while HCl and HNO_3 acids treated kaolin have more acidity.

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