



Preparation and characterization of adsorbents derived from bentonite and kaolin clays

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Received: 22 January 2018 / Accepted: 14 September 2018 / Published online: 10 October 2018
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Abstract

The comparative study on preparation and characterization of modified bentonite and kaolin clay types is aimed at establishment of the ability of these clay types to adsorb pollutants. Its low cost, availability and recovery of clay give it added advantage of an effective adsorbent. The modified clay types were prepared by impregnation using various concentrations of either H₂SO₄ or NaOH in w/v ratio of 1:2. The physicochemical and adsorptive properties were investigated using standard physicochemical methods like moisture content, bulk density, pH, iodine and methylene blue numbers. FTIR, XRD and SEM analyses were also conducted on these clay types. Unmodified kaolin clay exhibited lowest moisture content (1.12%) while unmodified bentonite clay type had highest value (3.98%). The peaks at 3435 cm⁻¹ and 3410 cm⁻¹ assigned N–H stretching frequency were obtained for 2 M H₂SO₄ modified and unmodified bentonite clay types, respectively. The peaks at 912 cm⁻¹ and 914 cm⁻¹ that indicate the presence of Al–Al–OH deformation frequency were obtained for unmodified bentonite clay type and 2 M H₂SO₄ modified bentonite clay, respectively. The physical surface morphology of the clay types revealed the presence of pores with irregular shapes, while their XRD analysis showed that the clay types are crystalline. The modified clay types exhibited better potential adsorbent for removal of small metallic or gas molecules as well as large organic molecules. Adsorbents could also remove cations or anions of pollutants since their surface charge could be positive or negative depending upon pH condition.

Keywords Bentonite clay · Kaolin clay · Adsorbent · Methylene blue number · Iodine number

Introduction

Clay as a natural scavenger of pollutant is important in the role of environment by taking up cations and anions either through ion exchange or adsorption or both. Thus, it contains exchangeable anions and cations on its surface such as Ca²⁺, Mg²⁺, H⁺, NH₄⁺, Na⁺, SO₄²⁻, Cl⁻ and NO₃⁻ which can be exchanged with other ions relatively without affecting the clay mineral structure. Due to clay's large specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC) and so on (Bergaya and Lagaly 2006), clays exhibit excellent adsorbent properties. Bronsted and Lewis type of acidity in clays (El-Bayaa et al. 2009) have also enhanced to great extent

the adsorption capacity of clay minerals. The Bronsted acidity arises by dissociation of water molecules of hydrated exchangeable metal cations on the surface, thereby forming H⁺ ions on the surface. If there is net negative charge on the surface, Bronsted acidity may arise due to the substitution of Si by Al³⁺ in some of the tetrahedral positions and H₃O⁺ cations that balanced the resultant charge. The exposure of trivalent cations mostly Al³⁺ at the edges, or Al³⁺ arising from rupture of Si–O–Al bonds, or through dehydroxylation of some Bronsted acid sites absorb anions, cations and nonionic and polar contaminants from natural water. The contaminants that saturate the clay surface could not easily be removed through the processes of ion exchange, coordination or ion–dipole interactions because pollutants can be held through H-bonding, Van der Waals interactions or hydrophobic bonding arising from either strong or weak interactions sometimes. The strength of the interactions is determined by various structural and other features of the clay mineral.

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Till date, several adsorbents such as porous carbon, biological, agricultural and industrial waste materials have been used to remove pollutants from wastewater but have one deficiency over each other (Elwakeel et al. 2017).

The aim of this research is to prepare and modify cheap, easily recovery alternative adsorbents for the removal of pollutant such as dyes, heavy metal and organic compounds from wastewater.

Materials and method

Geographical location of clay types

Kaolin clay was collected from the geographical location of Ijapo estate area of Akure in Ondo state, south–west region of Nigeria with longitude and latitude of 7°16'06.0"N and 5°12'17.1"E, respectively. While bentonite clay was collected from the geographical location of deposit of Afuze in Edo state, south–south region of Nigeria with longitude and latitude of 6°56'24.2"N and 5°59'07.7"E, respectively.

Preparation of the adsorbent

The collected bentonite and kaolin clay types were separately grounded into fine powder and sieved through a 0.25-mm mesh size to remove all the debris and further rinsed with water and oven-dried at 105 °C until all the moisture has evaporated.

Known amounts (50 g) of bentonite or kaolin clays from the above samples were separately added to 100 ml of 2 M, H₂SO₄ and NaOH, respectively. They were individually shaken vigorously using a uniscope SM101 shaker water bath for 24 h at 30 °C. They were separately washed with distilled water in order to remove the excess acid until effluent filtrate became neutral (pH = 7) (Abu-Ellella et al. 2015) and it was placed in a watch glass and oven-dried at 80 °C for 24 h.

Nomenclature of the samples

Unmodified bentonite clay was denoted as UBC, unmodified kaolin clay as UKC, 2 M H₂SO₄-modified bentonite clay as 2-ABC, 2 M H₂SO₄-modified kaolin clay as 2-AKC, 2 M NaOH-modified bentonite clay as 2-BBC and 2 M NaOH-modified kaolin clay was denoted as 2-BKC.

Characterization of the adsorbents

The modified and unmodified clay types were characterized for moisture content, bulk density, particle density, pH and

pH_{pzc} while the chemical and mineralogical compositions were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM) for functional group (Austin and Hoang 2009), structure (Ramachandran and Beaudoin 2008) and physical morphology (Mullan 2006) of the modified and unmodified clay types, respectively.

The chemical and mineralogical compositions were characterized by Fourier transform infrared (FTIR) using Perkin Elmer 1600 Series FTIR.

Physicochemical characterization of modified and unmodified clay types

Moisture content determination

Moisture content of each modified and unmodified clay types was carried out using standard method (ASTM 1996; Allen 1999), and it was conducted in triplicates. The loss in weight represents the moisture content of the sample and was calculated using the formula:

$$\%MC = \frac{X_g - Y_g}{X_g} \times 100$$

where X_g represents weight of sample before drying, Y_g represents weight of sample after drying and % MC represents percent of moisture content.

Bulk density determination

The bulk density of the modified and unmodified clay types was determined according to the procedure described by Ahmedna et al. (1997), Huerta-Pujol et al. (2010) and was conducted in triplicates. A little vibration was applied until no particle space and constant level of clay is noticed in the cylinder and the volume was recorded. The formula used is given as:

$$\text{Bulk density (g/dm}^3\text{)} = \frac{\text{Weight of clay}}{\text{Volume}}$$

Particle density determination

Particle density of each modified and unmodified clay types was carried out using standard method (ASTM 1996; Allen 1999), and it was conducted in triplicates and the particle density was calculated according to the formula:

$$\text{particle density} = \frac{\text{Weight of soil}}{\text{Volume of soil taken}} = \frac{W}{V_2 - V_1}$$

Determination of pH

The pH of the modified and unmodified clay types were determined by putting 10 g of each clay types into a 100-ml beaker and 20 ml of distilled water was added and stirred at 100 rpm for 30 min differently. Each clay-type pH was measured with the pH meter INOLAB pH 7310 (ASTM 1996; Allen 1999) and was done in triplicate.

Determination of porosity test using methylene blue and iodine number

Methylene blue (MB), a basic dye, was obtained from M and B laboratory chemicals in commercial purity percent and was applied without any further purification. A stock solution of this basic dye was prepared by weighing a quantity of 1.00 g of the dye in distilled water to make 1000 mg/L. Other various concentrations were prepared using serial dilution. Various concentrations of MB were determined by using the BECHMAN UV—visible spectrophotometer DU-640 (Chongrak et al. 1998) to measure the extent of porosity of each adsorbent. A calibration curve of optical densities against methylene blue concentrations was also obtained by using standard methylene blue solutions of known concentrations at pH value 7. This was done using 50 mg/L concentration to obtain the λ_{\max} of 664 nm.

The adsorption of aqueous iodine solution is considered as good adsorbate for evaluating the surface area of adsorbents such as activated carbon, agricultural wastes and mineral clays, associated with pores greater than 1 nm. Iodine number is accepted as the most fundamental parameter used to characterize adsorbent performance. It gives the measure of activity level (higher number indicates higher degree of activation). The iodine number is defined as the amount of iodine adsorbed per gram of activated carbon at an equilibrium concentration measured according to the procedure established by the American Society for Testing and Material ASTM 2006. A 0.1 g of dried raw and modified kaolin and bentonite clay types were taken in dried 100-ml different conical flasks. A 5 ml of 5% HCl was added. The flasks were then swirled until the adsorbents are wetted. A 10 ml of 0.1 N iodine solutions was added to each flask and shaken properly for 4 min and filtered. A 10 ml filtrate is then titrated against standard (0.1 N) sodium thiosulphate using starch as an indicator. The concentration of iodine adsorbed by adsorbents was calculated as amount of iodine adsorbed in milligrams.

Iodine number = $c \times$ conversion factor

c = Blank reading – volume of sodium thiosulphate consumed

The conversion factor can be calculated as follows:

$$\text{Correction Factor} = \frac{\text{Mol.wt of iodine} \times \text{normality of Iodine} \times 10}{\text{Wt.of adsorbents} \times \text{Blank reading}}$$

Determination of point of zero charge

Point of zero charge (PZC) is traditionally defined as the pH value where one or more components of the surface charge vanish at a specific temperature, pressure and aqueous solution composition. The PZC was determined by the pH method. It was accomplished by adding 0.1 g of the each of the adsorbents to 200 ml of 0.1 M NaCl differently to predetermine initial pH (pHi). The initial pH of NaCl solutions in different flasks to which the adsorbents were added was adjusted with 0.1 M NaOH or HCl to pH 1–12. The flasks were covered and shaken for 24 h after which the final (pHf) was measured using pH meter INOLAB pH 7310. A plot of change in pH (pHi–pHf) against the initial pH gives pH_{Zpc} where the plot crosses the horizontal axis (Ekpete and Horsfall, 2011).

Data handling

Statistical analysis such as Duncan was carried out on the data obtained using IBM SPSS 20 Package.

Instrumental characterization of the adsorbents

Fourier transform infrared (FTIR)

The surface functional group of each clay types was studied by Fourier transform infrared spectroscopy (FTIR). Each of the samples was prepared with KBr, and its tablet or pellet subjected under various characteristic chemical bonds (or stretching) was determined from which certain functional groups were derived (Socrates 1980; Austin and Hoang 2009).

X-ray diffraction (XRD)

A known quantity sample clay types were pulverized in a container and coated with tungsten carbide. Subsequently, a 7 g sample from the pulverized material was mixed with 1.4 g of organic wax and used to produce tablets for the determination of the chemical composition for each modified and unmodified clay types. These tablets were placed in Philips-P analytical PW 2400 equipment, operating with a rhodium X-ray source of 3 kW (Ramachandran and Beau-doin 2008).

Scanning electron microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that gives images of each clay type by scanning it with a focused beam of electrons. The electrons interact with atoms in each clay type giving various signals that

can be detected and that contain information about the clay type's surface morphology and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is mixed with the detected signal to produce an image. SEM can produce resolution better than 1 nm. Specimens can be observed in high vacuum, in low vacuum, in wet conditions (in environmental SEM) and at a wide range of elevated temperatures (Mullan 2006). This was carried out using high vacuum-based SEM SCOTECH 30000.

Result and discussion

Physicochemical characterization of modified and unmodified clay types

Table 1 shows the moisture content values of 3.98% and 1.12% obtained for UBC and UKC, respectively. They are related in the order of increment to the 3% and 5% reported for kaolin and bentonite by Ramesh (2014). The 2-ABC, 2-AKC, 2-BBC and 2-BKC are found to be 3.49, 1.4, 1.5 and 1.2%, respectively. Modification of the adsorbent did not seem to cause appreciable change to the moisture content of the adsorbents when their values are compared to their respective unmodified forms.

The bulk density of clay is the measurement of how dense and compact clay is. Table 1 shows the bulk density of the clay type had values of 1.42, 1.35, 1.10, 1.03, 1.80 and 1.86 g/ml obtained for UKC, UBC, 2-AKC and 2-ABC, 2-BBC and 2-BKC, respectively. The 2-BKC has the highest bulk density value of 1.86 g/ml among them all. These slightly varying values could be attributed to the variation in the organic constituents that make up the clay type and it has also reported in the literature that during the modification process involved in the production of adsorbent, the rate at which the starting material volatilizes, as well as hardness, strength are dependent on their starting material's bulk densities (Pendyal et al. 1999).

Clay particle density (g/cm^3) is the mass of clay solids (oven dry) per unit volume of clay. Clay particle density

depends on the densities of the various constituent solid and their relative abundance. The range is fairly narrow because common soil minerals but differ little in density. An average value of 2.65 g/cm^3 is often assumed. In contrast, organic soils mineral have lower particle densities since the density of organic matter is much less than that of mineral particle. From Table 1, the particle densities of the clay types are 2.50, 2.55, 2.67, 2.92, 2.16 and 2.43 g/cm^3 for UBC, UKC, 2-ABC, 2-AKC, 2-BBC and 2-BKC, respectively.

The pH of a clay type is a measurement of the degree of acidity or alkalinity of the clay. This gives an insight on the acidic or alkaline nature of the clay. It can be observed from Table 1 that the pH of the clay types is 7.5, 7.7, 6.48, 6.41, 8.48 and 8.7 for UKC, UBC, 2-ABC 2-AKC, 2-BBC and 2-BKC, respectively. It was revealed that UKC and UBC are slightly alkaline in nature while 2-AKC and 2-ABC are acidic while 2-BBC and 2-BKC are basic in nature. The pH values for the pretreated clay samples are closer to pH 7.2 reported by Ramesh (2014).

pH point of zero charge of adsorbents prepared from these bentonite and kaolin clays was determined. The values were known by determining the point where the resulting curve cut through the pHo axis as shown in Fig. 1. The pH_{pzc} was found to be 6.2, 8.9, 7.0, 3.7, 7.8 and 7.8 mmol/g for UBC, UKC, 2-ABC, 2-AKC, 2-BBC and 2-BKC, respectively. The influence of all the functional group present in each sample determines pH_{pzc}, the pH at which the net surface charge on each sample is zero. At $\text{pH} < \text{pH}_{\text{pzc}}$, the sample surface has a net positive charge, while at $\text{pH} > \text{pH}_{\text{pzc}}$, the surface has net negative charges (Bello et al. 2016). Anion adsorption becomes to enhance at lower pH than the pH_{pzc} while adsorption of cations is also enhanced at pH higher than pH_{pzc} (Bello et al. 2016).

Methylene blue and iodine number were carried out to determine the adsorption capacity of these various clay types. From the results in Table 2, adsorption of methylene blue solution for UBC, 2-ABC, 2-BBC, UKC, 2-AKC and 2-BKC were found to be 0.7, 76.58, 174.8, 175.2, 92.58 and 31.1 mg/g, respectively, while the result for iodine

Table 1 Physicochemical properties of various adsorbents with Duncan multiple range test data

Properties	UBC	2-ABC	2-BBC	UKC	2-AKC	2-BKC
Moisture content (%)	3.98 ± 0.4^d	3.49 ± 0.4^d	1.5 ± 0.7^{ab}	1.12 ± 0.5^a	1.4 ± 0.6^{ab}	1.2 ± 0.4^a
Bulk density (g/ml)	1.35 ± 0.1^d	1.03 ± 0^{ab}	1.8 ± 0^e	1.42 ± 0^e	1.1 ± 0^a	1.86 ± 0.2^e
Particle density (g/ml)	2.50 ± 0^{cd}	2.67 ± 0^f	2.16 ± 0^{bc}	2.55 ± 0^{de}	2.92 ± 0^g	2.43 ± 0.1^c
pH	7.7 ± 0^e	6.48 ± 0^b	8.48 ± 0^h	7.5 ± 0^d	6.41 ± 0^b	8.7 ± 0^i
pH _{pzc}	6.2	7.0	7.8	8.9	3.7	7.8

The results represent mean \pm standard deviation of triplicate determination; using Waller Duncan, similar letters along the same row represent no significant statistical difference in parameter at 95% probability while those with different letters are significantly different as per modification variables

Fig. 1 Plot of pH_{pzc} of UKC, UBC, 2-AKC, 2-ABC, 2-BKC and 2-BBC

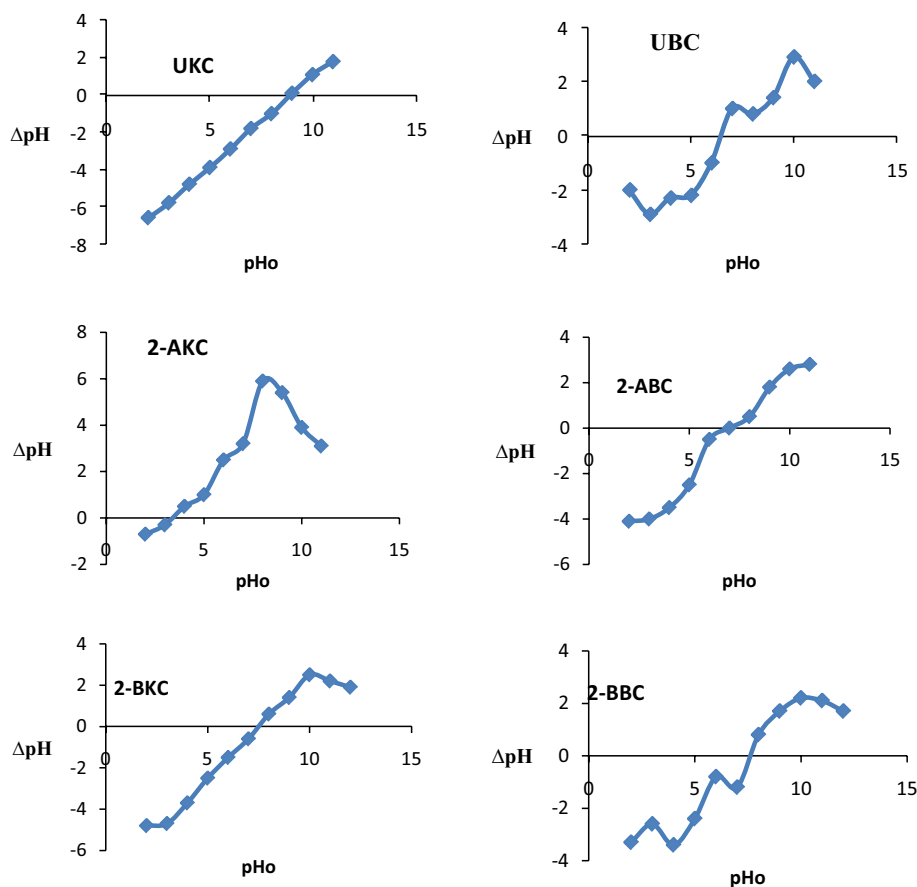


Table 2 Methylene number and iodine number values

Sorbent	q_e (mg/g)	%R	IAN
UBC	0.7 ± 0.071	0.39	850.97
2-ABC	76.58 ± 0.11	42.45	1264.10
2-BBC	174.8 ± 0.14	96.87	1264.10
UKC	175.2 ± 0.11	97.10	1283.96
2-AKC	92.58 ± 0.11	51.32	1325.92
2-BKC	31.1 ± 0.071	17.24	1445.26

The results of the amount adsorbed q_e represent mean \pm standard deviation of triplicate determination

number is as follows: 850.97, 1264.10, 1264.10, 1283.96, 1325.92 and 1445.26 mg/g are for UBC, 2-ABC, 2-BBC, UKC, 2-AKC and 2-BKC, respectively. It revealed that modification followed by acid and bases had a significant influence on creation of various pores sizes of the samples. Comparing these results with other literature values, it was observed that these sorbents give more yields than groundnut shell, sheanut, poultry dropping and poultry waste sorbents (Itodo et al. 2010).

Instrumental characterization of unmodified and modified clay types

FTIR spectra of unmodified and modified bentonite and kaolin clay types

Figure 2 shows the FTIR spectra of UKC, 2-ABC, 2-BBC, UBC, 2-AKC and 2-BKC, respectively. The spectra of the samples show the presence of several functional groups. These spectra revealed a reduction, broadening, disappearance or appearance of new peaks after the process of modification. The shifts in the spectra revealed the effect of modification. The prominent bands after modification show that the prepared adsorbents will be effective in the removal of heavy metal and dyes.

The sharp bands at 3696.17 cm^{-1} and 3626.39 cm^{-1} are attributed to the N–H stretching for the UBC and 2-ABC types as it is the same as the peaks at 3697 and 3620 cm^{-1} reported by Georges–IVO (2005). The peaks at 3436.41 cm^{-1} in the 2-ABC sample and 3430.21 cm^{-1} in the UBC are assigned to OH stretching which is close to 3426 cm^{-1} and 3420 cm^{-1} reported by Isci et al. (2006), Aroke et al. (2013). The bands 1644.47 cm^{-1} and 1637.99 cm^{-1} are present in UBC and 2-ABC samples and

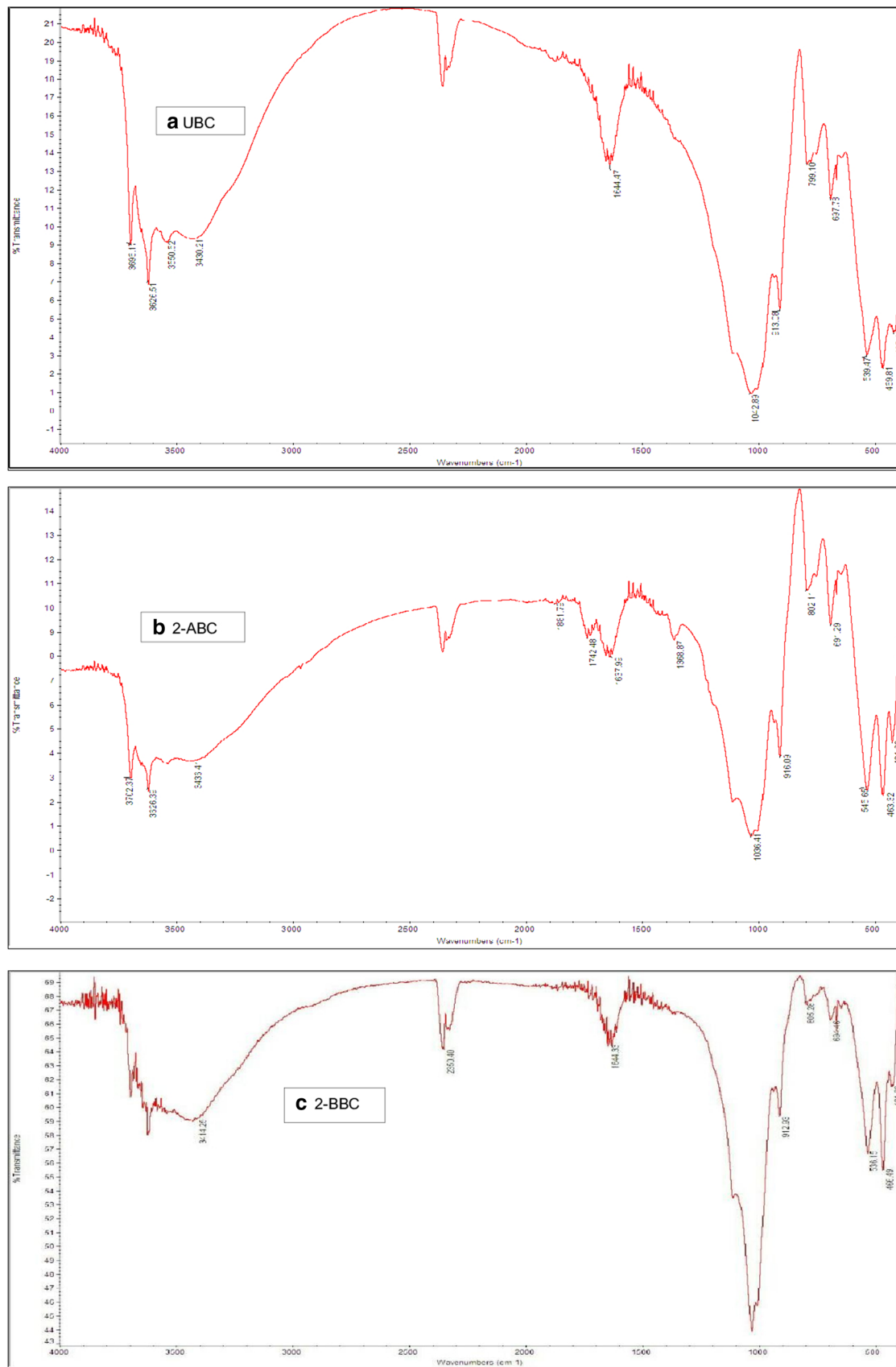


Fig. 2 FTIR spectra of a UBC, b 2-ABC, c 2-BBC, d UKC, e 2-AKC and f 2-BKC, respectively

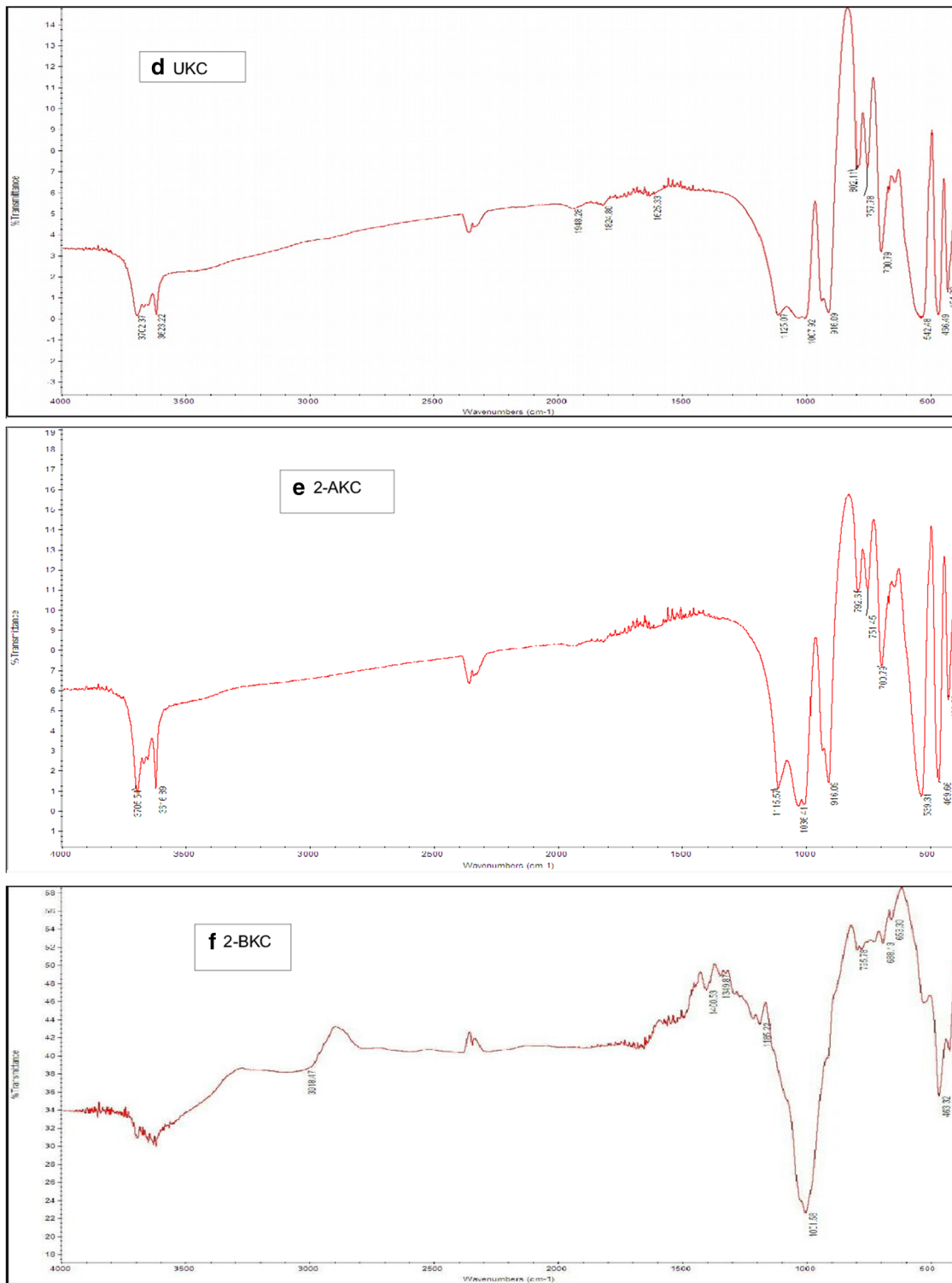


Fig. 2 (continued)

are assigned to the H–O–H bending of water which fits within range reported at peaks 1620–1642 cm⁻¹ (Bhasker and Gopalakrishnarao 2010). The peaks observed at

1042.89 cm⁻¹, 1036.41 cm⁻¹ and 1029.58 cm⁻¹ are assigned to the characteristic bands of silicate which are greatly related to the stretching vibrations of Si–O and

Table 3 BET parameter analysis

Parameters	2-AKC	2-BBC
Pore volume (cm ³ /g)	0.411	0.234
Surface area (m ² /g)	141.4	233.7
Pore size distribution (nm)	1.324	1.324

they agree to that noticed at 1150 cm⁻¹, 1060 cm⁻¹ and 1030 cm⁻¹ which were reported by Aroke et al. (2013). The peaks at 913.08 cm⁻¹, 916.09 cm⁻¹ and 912.55 cm⁻¹ are responsible for Al–Al–OH group deformation and are similar to those of 913 cm⁻¹ and 914 cm⁻¹ reported by Amin et al. (2010).

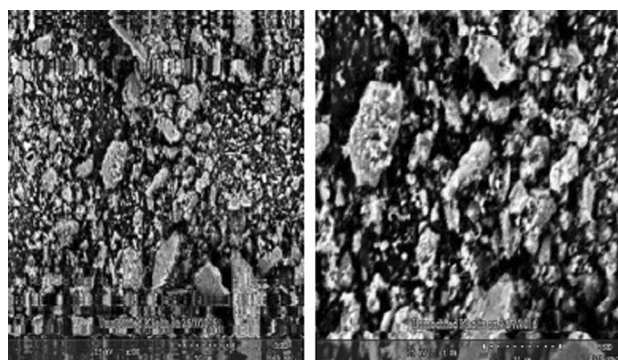
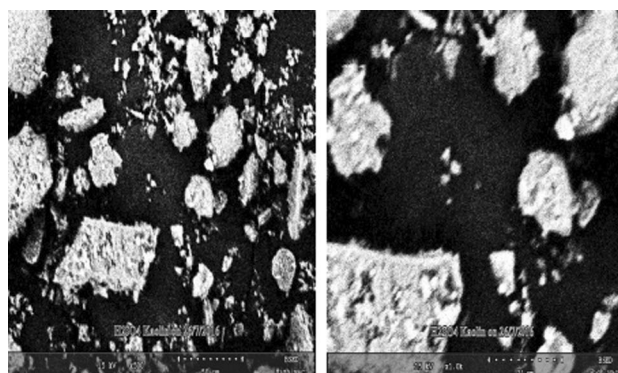
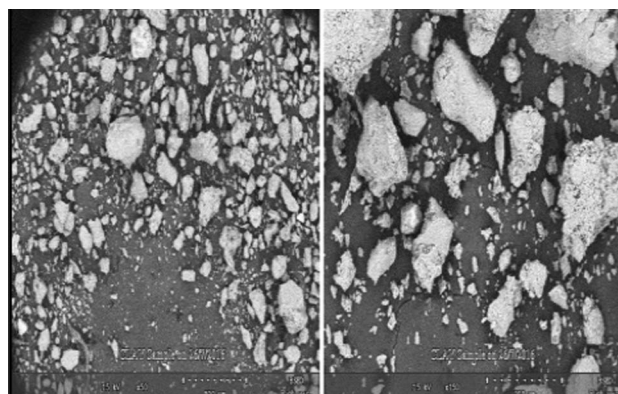
The sharp peaks at 3623.22 cm⁻¹ and 3702.31 cm⁻¹ were ascribed to the inner surface N–H stretching and inner hydroxyl group with higher amount of Al–OH in the octahedral sheet, respectively. These peaks are the same with those reported by Georges–IVO (2005) at 3697 and 3620 cm⁻¹, respectively. The peaks 1625.33 cm⁻¹ are assigned to the H–OH bending of water and this closely agree to 1620–1642 cm⁻¹ (Bhasker and Gopalakrishnarao 2010). The peaks at 1036.41 cm⁻¹ and 1007.92 cm⁻¹ are ascribed to the Si–O deformation bands which are closer to that reported by Georges–IVO (2005) at 1033, 1032 and 1007 cm⁻¹. The peaks 912–937 cm⁻¹ were ascribed to Al–OH bending vibration of kaolin clay type and are closer to that of 914–936 cm⁻¹ range (Bhasker and Gopalakrishnarao 2010). The peaks at 799.10 cm⁻¹, 757.78 cm⁻¹ and 797.78 cm⁻¹ were assigned to the Si–O stretching of the kaolin clay type. These peaks agreed to that reported at 796 cm⁻¹, 754 cm⁻¹ and 695 cm⁻¹ (Georges–IVO 2005) and are close to the value of bands for theoretical kaolin clay type, defined as pure kaolin clay with the chemical formula Al₂Si₂O₅(OH)₄.

SEM micrograph of unmodified and modified for kaolin and bentonite clay types

Figures 6, 7 depict the monographs of SEM of the clay types.

XRD spectra for acid-modified and base-modified bentonite clay

Figures 3, 4, 5, 6 and 7 depict the SEM micrographs at ×500 and ×1000 magnifications for UKC, 2-AKC, UBC, 2-ABC and 2-BBC, respectively. They revealed numerous pores with irregular shapes, rough, uneven which indicated much contact area and easy pore diffusion during adsorption (Patel and sudhakar 2008). The XRD powder analysis for 2-ABC, 2-BBC and UKC, respectively, is presented in Fig. 8a–c.

**Fig. 3** SEM micrograph of UKC at ×500 and ×1000 magnifications**Fig. 4** SEM micrograph of 2-AKC at ×500 and ×1000 magnifications**Fig. 5** SEM micrograph of UBC at ×500 and ×1000 magnifications

There is a conspicuous peak at 2θ equal 18°, 2θ equal 18° and 2θ equal 22° for the 2-ABC, 2-BBC and UKC, respectively, and showed that they are crystalline in nature.

The surface area, pore volume and pore size distribution are calculated from the initial plot of amount of N₂ gas

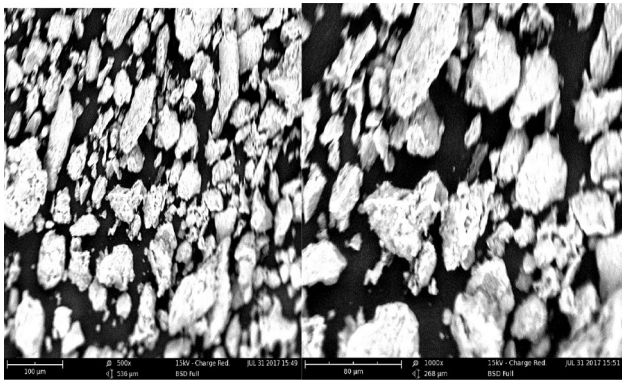


Fig. 6 SEM micrograph of 2-ABC at $\times 500$ and $\times 1000$ magnifications

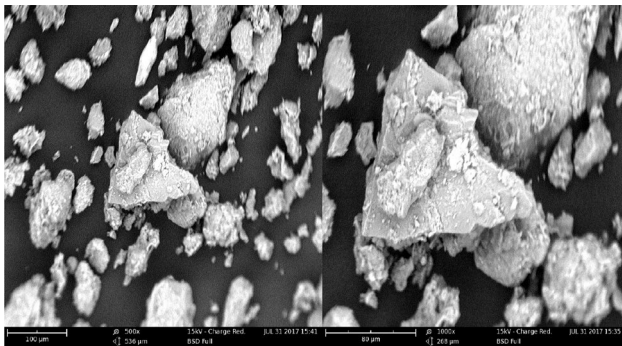


Fig. 7 SEM micrograph of 2-BBC at $\times 500$ and $\times 1000$ magnifications

adsorbed at STP against the relative pressures, P/P_0 within the range of 0–3.2 for both 2-AKC and 2-BBC.

A surface area of $233.7 \text{ m}^2/\text{g}$ and pore volume ($0.234 \text{ cm}^3/\text{g}$) obtained for 2-BBC are greater than surface area ($141.4 \text{ m}^2/\text{g}$) and pore volume ($0.411 \text{ cm}^3/\text{g}$) of 2-AKC.

These values are within the minimum range of $100\text{--}1500 \text{ m}^2/\text{g}$ needed for industrial application and removal of small molecules from the pore size distribution (1.324 nm) obtained for 2-AKC could be classified as microporous.

The physical observation of 2-AKC is similar to that of commercial granular active carbon (CGAC) which showed the initial fast adsorption rate. However, most average active carbon samples micropore volumes are generally between 0.2 and $0.5 \text{ cm}^3/\text{g}$ with surface area up to about $1000 \text{ m}^2/\text{g}$ (Grajek 2000). It has been reported that total pore volume in the range of $0.3\text{--}0.8 \text{ cm}^3/\text{g}$ of active carbon derived from olive stones is often used as precursors for high-grade active carbon (Linares-Solano et al. 1984) (Table 3).

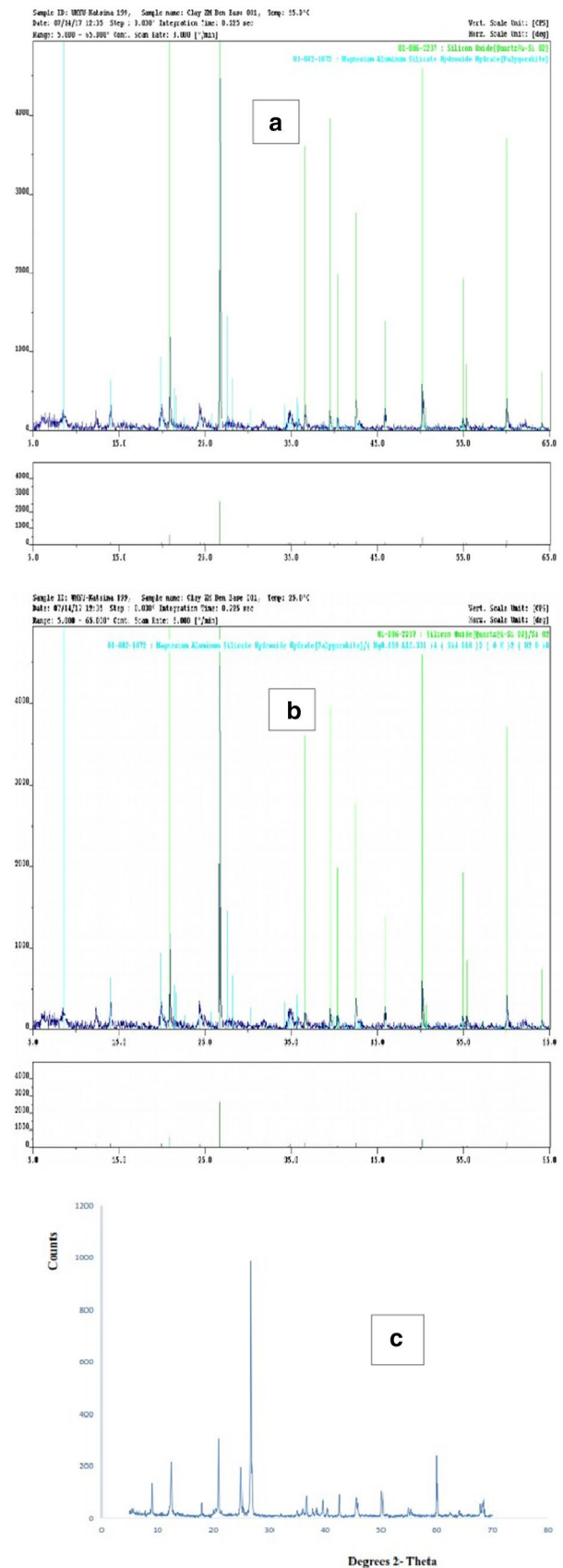


Fig. 8 XRD spectra of a 2-ABC, b 2-BBC and c UKC

Conclusion

This study revealed that modification of bentonite clay and kaolin clays was effective in creating well-developed pores on the surface. Various level of degree of adsorption was achieved on methylene blue and iodine molecules. The amounts of methylene blue adsorbed by these various adsorbents were strongly influenced by their adsorption capacities. The surfaces of studies samples are acidic and neutral which indicate a promising ability to remove different pollutants such as dyes, metal ions and other organic pollutants. There is further ongoing research to observe the best among all these potential adsorbents. Thus, there is high potential ability for some of these potential adsorbents to be utilized for removal of different degree of sizes of molecule either in gas, small molecules or bigger molecules which are pollutant in our environment when compared with other low-cost adsorbents.

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References

- Abu-Elella R, Ossman M, Farouq R, Abd-Elfatah M (2015) Used motor oil treatment: turning waste oil into valuable products. *Int J Chem Biochem Sci* 7:57–67
- Ahmedna M, Johnson M, Clarke SJ, Marshall WE, Reo RM (1997) Potential of agricultural by-products based activated carbon for use in raw surge decolorization. *J Sci Food Agric* 75(1):117–124. [https://doi.org/10.1002/\(sici\)10970010\(199709\)75:1%3c117::AID-JSFA850%3e30.CO;2-m](https://doi.org/10.1002/(sici)10970010(199709)75:1%3c117::AID-JSFA850%3e30.CO;2-m)
- Allen RF (1999) Standard test methods for determining average grain size (F112). Annual book of ASTM standards, metal-mechanical testing; elevated and low temperature tests; metallography
- Amin E, Khairul A, Hadi N (2010) Physicochemical characteristics of phosphoric acid stabilized bentonite. *Electron J Geotech Eng* 15c:327–336
- Aroke U, Abdulkarim A, Ogunbunke R (2013) Fourier transform infrared characterization of kaolin, granite, bentonite and barite. *ATBU J Environ Technol* 6:1
- ASTM (2006) Standard test method for determination of iodine number of activated carbon. D4607–94
- Austin E, Hoang KT (2009) Evaluation of gasmet TM DX-4015 series Fourier transform infrared gas analyzer, DTIC Document
- Bello OS, Owojuyigbe ES, Babatunde MA, Folaranmi FE (2016) Sustainable conversion of agro-waste into useful adsorbents. *J Appl Water Sci*. 04:94–100. <https://doi.org/10.1007/s13201-016-0494-0>
- Bergaya F, Lagaly G (2006) General introduction: clays, clay minerals, and clay science. *Dev Clay Sci* 1:1–18. [https://doi.org/10.1016/S1572-4352\(05\)01001-9](https://doi.org/10.1016/S1572-4352(05)01001-9)
- Bhasker JS, Gopalakrishna P (2010) Fourier transform infrared spectroscopic characterization of kaolinite from Assam and Maghalaya, Northeastern India. *J Mod Phys* 1:206–210. <https://doi.org/10.4236/jmp.2010.14031>
- Chongrak K, Erich H, Nouredine A, Jean P (1998) Application of methylene blue adsorption to cotton fiber specific surface area measurement. *J Cotton Sci* 2:164–173
- Ekpete OA, Horsfall MJ (2011) Preparation and characterization of activated carbon derived from fluted pumpkin stem wastes (*Telfairiaoccidentalis Hook F*). *Res J Chem Sci* 1(3):10–17
- El-Bayaa AA, Badawy NA, Alkhalik EA (2009) Effect of ionic strength on the adsorption of copper and chromium ions by vermiculite pure clay mineral. *J Hazard Mater* 170(2):1204–1209. <https://doi.org/10.1016/j.jhazmat.2009.05.100>
- Elwakeel KZ, Elgarahy AM, Mohammed SH (2017) Use of beach bivalve shells located at Port Said coast (Egypt) as a green approach for methylene blue removal. *J Environ Chem Eng* 5(1):578–587
- Georges-IVO EE (2005) Fourier transform infrared spectrometry and X-ray powder diffraction as complementary techniques in characterizing clay size fraction of kaolin. *J Appl Sci Environ Manag* 9(2):43–48. <http://hdl.handle.net/1807/6452>
- Grajek H (2000) Regeneration of adsorbents by use of liquid subcritical and supercritical carbondioxide. *Adsorpt Sci Technol* 18(4):347–371. <https://doi.org/10.1260/0263617001493486>
- Huerta-Pujol O, Soliva M, Martinez-Farre F, Valero J, Lopez M (2010) Bulk density determination as a single and complementary tool in composting process control. *Biores Technol* 101(3):995–1001. <https://doi.org/10.1016/j.biortech.2009.08.096>
- Isci S, Unlu C, Atici O, Gungor A (2006) Rhelogy and structure of aqueous bentonite ployvinyl alcohol dispersion. *J Indian Acad Sci*. 29(5):454–456. <https://doi.org/10.1007/BF02914075>
- Itodo AU, Abdulrahman FW, Hassan LG, Maigandi SA, Itodo HU (2010) Application of methylene blue and iodine adsorption in the measurement of specific surface area by four acid and salts treated activated carbons. *NY Sci J* 3(5):25–33
- Linares-Solano A, Rodriguez-Reinoso F, Molina-Sabio M, Lopez-Gonzalez JD (1984) The two stages air-CO₂ activation in the preparation of activated carbons. II characterization by adsorption from solution. *Adsorpt Sci Technol* 1(3):223–234. <https://doi.org/10.1177/026361748400100305>
- Mullan D (2006) Scanning electron microscopy 1928–1965. *Scanning* 17(3):175–185. <https://doi.org/10.1002/sca.4950170030>
- Patel JB, Sudhakar P (2008) Adsorption of mercury by powdered corn cobs. *Electr J Environ Agric Food Chem* 7(14):2735–2742
- Pendyal B, John MM, Marshall WE, Ahmedna M, Rao RM (1999) The effect of binders and agricultural by products on the physical and chemical properties of granular active carbons. *Biores Technol* 68:247–254. [https://doi.org/10.1016/S0960-8524\(98\)009](https://doi.org/10.1016/S0960-8524(98)009)
- Ramachandran VS, Beaudoin JJ (2008) Handbook of analytical techniques in concrete science and technology: principles, techniques and applications. William Andrew, Norwich, pp 564–573
- Ramesh KC (2014) Reduction of expansive index of kaolinite and bentonite clay using sand and fly ash mixture. Southern minois university at Carbondale, p 146
- Socrates G. (1980) Infrared characteristic group frequencies, vol. 30 no.4 Wiley, Chichester-Toronto, pp 1271–1277

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