Determination of Surface area of local silica via different methods

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Abstract

The surface area of a local silicate rock was investigated using different methods after being thermally treated at 200, 400,600 and 800 C° to detect the optimum temperature of treatment. The study has disclosed that the optimum temperature of treatment was 600C° for its maximum surface areas as compared to others. The surface area of the thermally treated samples was determined by many methods including retention by ethylene glycol mono ethyl ether (***EGME***), adsorption from solution using ***PNP*** and ***MB*** as solutes as well as the adsorption from vapor phase using acetone vapor. These samples, however, exhibited good surface areas as compared to the untreated silicate .Also, the adsorption isotherm of ***PNP*** and ***MB*** of all samples were determined and found to be fit to Langmuir type of isotherm which refers to clear micro porous tendency.

الخلاصة

في هذا البحث، تم دراسة تأثير المعالجة الحرارية عند درجات حرارية مختلفة على الصفات الامتزازية والمساحة السطحية لصخرة السليكات المحلية(بورسلينات). تمت المعالجة الحرارية للبورسلينات عند 800،600،400،200 م لمعرفة الدرجة الحرارية المثلى للمعالجة. وقد اثبتت هذه الدراسة ان المعالجة عند 600 م هي المعالجة الحرارية المثلى لأنها أعطت أعلى مساحات سطحية بالمقارنة مع النماذج الأخرى المعالجة حرارياً. المساحة السطحية للنماذج المعالجة حرارياً قد تم قياسها بعدة طرق منها امتزاز (EGME) والامتزاز من المحلول باستخدام PNP و MB كمحاليل ممتزة بالإضافة إلى الامتزاز من الطور البخاري باستخدام بخار الاسيتون. وقد اظهرت النماذج المنشطة مساحة سطحية جيدة مقارنة بالسليكا غير المعاملة حرارياً. ولقد تم أيضا تعيين ايزوثرمات الامتزاز للنماذج المعاملة حرارياً باستخدام مادتي PNP و MB كمواد ممتزة وأظهرت هذه الايزوثرمات تطابقها مع النوع لانكمير(نوع L) من ايزوثرمات الامتزاز والتي تشير إلى المسامية الدقيقة للنماذج.

Introduction

The adsorption of organic molecules on clay surfaces has been extensively studied. On the other hand, adsorption of cationic dyes on clay minerals has been widely used as the basis for staining tests and identification. The interactions between charged organic molecules and clays play an important role in determining the environmental behavior of certain organizations, some of which exhibits herbicidal properties. Many workers have shown that clay has the ability to reduce drastically the effects of herbicides [1].

Although the BET method is not commonly used in soil science for surface area determinations but the sorption of vapors that may penetrate into the interior of the bulk solid is also known. Retention method of ethylene glycol mono ethyl ether (***EGME)*** has been to determine total surface area of some clays such as montmorillonite .The discrepancy between total surface area by the retention method and BET N_2 method is considered to be (internal surface areas). In contrast to BET model, these internal surface areas are created by the experiment, and their values may be expected to vary widely with different sorbates ,Other adsorption techniques used in surface area determination of fine grained powders, such as activated carbon and silica gel includes adsorption from solution technique which was suggested by Giles et.al. Adsorption studies have been described with fatty acids, aromatics, esters and dyestuff [2-4].

The studied silicate is locally known as "Ninavite" which is characterized by a white color and vary low density ($\simeq$ 0.38 g/cm^3). It consists mainly of x-ray amorphous silica phases ($SiO_2.nH_2O$) (A, Opal ET)) which forms about 95% of the studied samples with small amounts of quartz (<2%) , gypsum (1.8%) and alunite (~1.5%) [5].

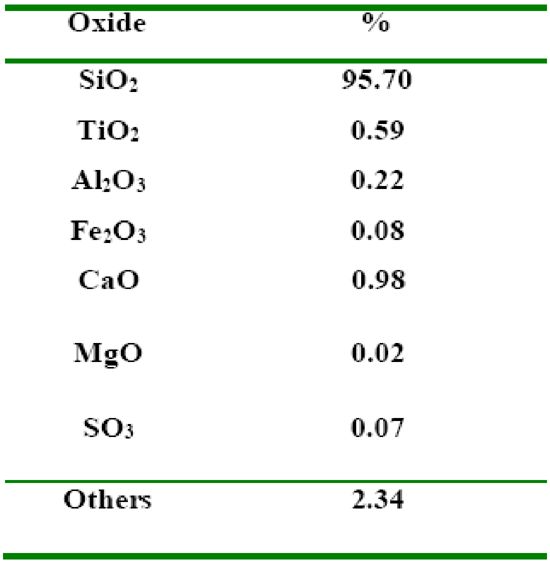
The main purpose of this paper is to study the effects of thermal treatment on the surface area of the studied silicate. Many methods have been used for surface area determination including retention method using ethylene glycol mono ethyl ether (***EGME***) , vapor phase adsorption using acetone vapor as well as adsorption from solution technique using ***PNP*** and ***MB*** as solutes.

Experimental

Adsorbent treatment

The silicate which is used as adsorbent was collected from the village of Al-Humairah, south of the city of Mosul, north of Iraq. Table 1 shows the chemical analysis of Ninavite[5].

Table 1. Chemical analysis of Ninavite.



Oxide	%
SiO_2	95.70
TiO_2	0.59
Al_2O_3	0.22
Fe_2O_3	0.08
CaO	0.98
MgO	0.02
SO_3	0.07
Others	2.34

The sample was ground at first and sieved by 20-40 mesh. Then is treated with concentrated HCl to remove some impurities such as alunite and gypsum and washed by distilled water many times to remove acid traces and finally was exposed to air for drying.

Four batches, each weighing (10) grams were thermally treated at different temperatures (200,400,600 and 800 C°) by means of a tubular muffle furnace for 2hrs to obtain the activated silicate. Thermally treated samples were labeled as follows (S_{200} S_{400}, S_{600}, and S_{800}).

Surface area determination:

The surface areas of the thermal treated samples were determined using three methods including:

Determination of the surface area by adsorption from vapor phase:

The used method is a gravimetric one, and based on passing a saturated dry air with acetone vapor through a bed of the adsorbent under atmospheric pressure. The adsorption process went on till a constant mass was obtained which was detected by a four digit balance (0.0001 mg) which represents the monolayer of the adsorbate [6]. The following equation was used to calculate the surface area of silicate:

$$S_A = Vm.\ N.\ \sigma \text{ .... } (1)$$

Where, **Vm** is the volume required to form a monolayer on adsorbent surface ml/g, N is the Avogadro's number and σ is the cross sectional area of acetone molecule (0.165 nm^2). The use of acetone as adsorbate for this purpose belongs to its high vapor pressure at room temperature.

Determination of the surface area by retention method (EGME method):

The procedure includes wetting a sample with ***EGME***, equilibrating, and then removing the excess liquid by evacuation. The sample was removed periodically and weighed until a constant mass was obtained. The specific surface area was calculated from the mass of the retained liquid assuming that a monomolecular layer of ***EGME*** was adsorbed on the surface. The procedure applied in this work was done according to Lutengger method[7-8]. Surface area by retention method (***EGME***) [7-8], has been used by large number of investigators, the following equation is used for calculating the SA:

$$S_{SA} = W_a / 0.000286\ W_s \text{ .... } (2)$$

Where, SSA is the specific surface area in m^2/g, W_a is the weight of ***EGME*** retained by the sample in grams (sample –Ws), 0.000286 is the weight of ***EGME*** required to form a mono layer on a square meter of surface (g/m^2) and W_s is the weight of sample added (g).The SSA values of ***EGME*** adsorption of the studied sample are given in Table 2.

Table 2. **Surface area values of the thermally treated silicate samples.**

Sample	SA$_{EGME}$ m^2/g	SA$_{Acetone}$ m^2/g	SA$_{PNP}$ m^2/g	SA$_{MB}$ m^2/g
S	386	250	73	89
S$_{200}$	399	370	119	117
S$_{400}$	403	376	165	130
S$_{600}$	490	408	201	165
S$_{800}$	397	368	173	164

Table 3.

Sample	S$_{acetone}$/S$_{EGME}$	S$_{PNP}$/S$_{EGME}$	S$_{MB}$/S$_{EGME}$
S	64.7	18.91	23.05
S$_{200}$	92.77	29.82	29.32
S$_{400}$	93.3	40.94	32.25
S$_{600}$	83.2	41.02	33.67
S$_{800}$	92.6	43.57	41.30

Determination of the surface area by adsorption from solution method:

Adsorption from solution method was used by many of investigators [2-3,6] to determine the specific surface area of fine solids such as active carbon and silica gel using ***MB*** and ***PNP*** which are the most common solutes. A known weight (0.1g ± 0.001mg) of each sample was kept into a desiccators to avoid adsorbing any humidity from the atmosphere was agitated with a known volume (25ml) of solute solutions of different concentrations ranging from (5-50 mg/L ***PNP***) or (2-20 mg/L ***MB***) into a Stoppard conical flask at room temperature until equilibrium was obtained that is after 24hrs. The concentration of the supertant liquid was determined spectrophoto- metrically at a wavelength of 318 and 661 nm for ***PNP*** and ***MB*** respectively.

The amount of dye adsorbed on the sample Qe (mg/g) was calculated by mass balance relationship using equation. (3):

$$Q_e = [C_o - C_e]\, V / W \,\ldots\ldots\ldots (3)$$

Where C_o and C_e are the initial and equilibrium liquid phase concentrations, respectively (mg/L), V the volume of the solution and W the weight of the sample used (g). The linear form of Langmuire equation which is valid for monolayer sorption onto a surface was used for determining the amount which represents the monolayer adsorption Q_m as expressed in Eq. (4):

$$C_e / Q_e = 1/ K_L Q_m + C_e / Q_m \,\ldots\ldots(4)$$

Where Q_m is the amount adsorbed per unit mass of adsorbent corresponding to complete monolayer coverage on the surface bound at high C_e and K_L is the constant related to the affinity of binding sites. Surface area determination method via adsorption from solution requires samples use of *PNP* and *MB* as solutes since they are the most common solutes used for this purpose and the following equation is used for SA calculation:

$$SA_{Dye} = Q_m \,.\; N \,.\; \text{Ơ} \,/\, n \,\ldots\ldots (5)$$

Where SA_{Dye} is the surface area related to dyestuff in (m^2/g), Q_m is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage of the adsorptive sites and determined from Langmuire linear plots of PNP and MB on the silicate samples, (Figure 2 shows these plots). N is the Avogadro's number, σ is the cross sectional area of solute in (nm^2) which equals to 1.2nm^2 for ***MB*** and 0.52 nm^2 for ***PNP*** and *n* is the aggregation factor [1-4,6,12-13].

X-ray diffraction measurements:

X-ray diffraction (XRD) analyses were carried out using a Philips vapor 1430 differentiation. A dried sample of the produced material is ground using a mortar and pestle and tested at 40kV and40mA. The spectra was analyzed using PC-APD diffraction software.

Adsorbates:

Adsorbates used in this study are Methylene blue (***MB***), p-nitro phenol (***PNP***) and Ethylene glycol monoethyl ether(***EGME***) were supplied by BDH and Fluka with purity 99% and used without any further purification. Deionized water was used for dissolving ***MB and PNP.***

Results and Discussion

Effect of activation temperature

The silicate was thermally treated at different temperatures as was stated earlier. The treatment was accompanied by a loss in weight as can be seen in Figure (1). It can be seen from Figure1 that the increase of treatment temperature was accompanied by a loss in weight which could be attributed to the removal of H_2O molecules from silicate surface. This is for thermal treatment leads to abstracting a water molecule form two adjacent hydroxyl groups[9].

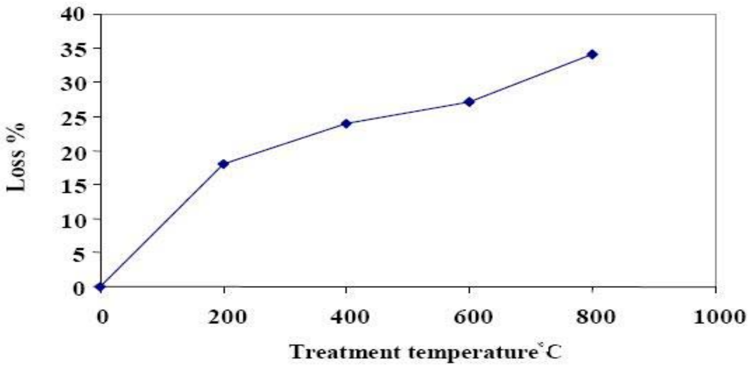


Figure 1. Relation between treatment temperature and loss%.

Specific Surface Area (SSA) measurements:

The surface areas of the silicate (S) and thermally treated samples using all adsorbates suggest that the sample has different pore size distribution. The enhancement of the surface area values however is clearly due to thermal treatment.

Determination of SA via solution adsorption was used for the first time for solid adsorbent by Giles et.al. [4], who used ***PNP*** and ***MB*** for this purpose. The adsorption of ***MB*** is a good test for adsorbents toward removing colors from their aqueous solutions. Adsorption of MB molecule is a measure of adsorbent ability to adsorb molecules of wider microspores (mesopores) [4-6,11,20].

The adsorption of ***PNP*** for SA evaluation is recommended to be suitable for a wide variety of solids, both porous and nonporous, provided that they either forms hydrogen bond with PNP or have aromatic nuclei [4]. The adsorption of ***PNP*** **is** another test for micro porosity [4-6, 11, 20] since this molecule measures the microspores to a value of (0.52) nm^2. Surface areas of the studied samples are given in Table2. Increasing thermal treatment temperature was accompanied by an increase in the SA values for both ***PNP*** and ***MB*** and suggests that thermal treatment enabled to enhance porous structure of the silicate, but the reason for the $\boldsymbol{SA_{MB}}$ to give lower values than $\boldsymbol{SA_{PNP}}$ could be due to the adsorption of certain dyes such as *MB* from aqueous solutions was formerly considered to be physical only. It is known that with cationic dyes such as ***MB*** at least, cation exchange first occurs, giving the way to physical adsorption only when complete replacement of the original ions by basic dye ions has occurred [3-4]. Giles et al. found that monatomic dyes form monolayers of ionic micelles when adsorbed at a solid surface. The average number of ions per micelle depends only on the ionic weight of the dye, while the adsorption of ***PNP*** doesn't involve micelle formation, but it was reported that the *O'* value must be doubled when a ***PNP*** monolayer is adsorbed onto the interlayer region of swelling clay minerals. [14].

Langmuire linear isotherms of ***PNP*** and ***MB*** are depicted in Figure 2, while their adsorption isotherms of both ***PNP*** and ***MB*** are shown in Figure 3, these isotherms was found to fit Longmuir type of isotherm according to Giles classification system for adsorption from solution [4]. The samples showed L type for ***MB*** and H type for ***PNP*** types of isotherms. What can be seen from ***MB*** adsorption isotherm that most of them had (L2 type). In this type of isotherm, the adsorbed quantity increases with the increment of ***MB*** concentration but then it becomes fixed which may mean that the adsorption sites have filled before the adsorption takes place may be due to the aggregation effect and the increase in concentration is useless. The adsorption isotherms of ***PNP*** which showed H type shows that the increasing of ***PNP*** concentration was accompanied by an increase in the adsorbed quantities until it reaches a constant quantity and then returns to increase again ,this means there is an affinity between the adsorbent and solute [3].

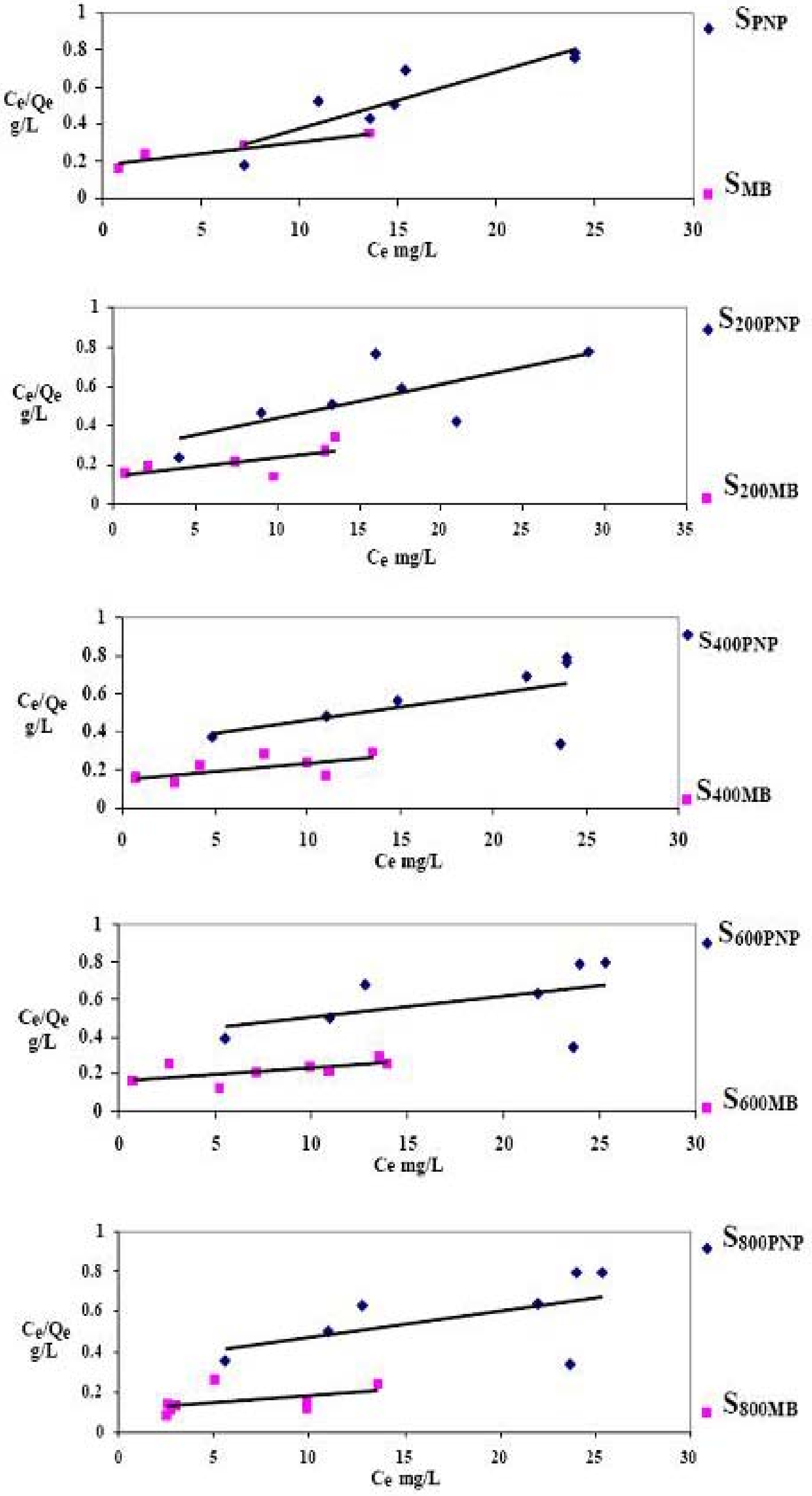


Figure 2. .angmuir linear plots of PNP and MB of the studied samples at 298K.

In comparison with some results obtained by Oguz and Fatma who also used this technique and the same solutes for determining ***SA*** of some Turkish silicates (Sepiolite, Zeolite and Kaolin), it can be seen that most of our samples were better than theirs, since both the silicate and thermally treated samples gave higher values than those reported by Oguz and Fatima[1]. This means samples of the present study are more porous than some Turkish silicates.

Since the vapor adsorption is an important process influencing the migration and the fates of many organic pollutants in the environment, therefore, the adsorption of acetone vapor for ***SA*** determination is a favorite since this substance was used by Mark for determining the SA of activated carbons [15]. The values are listed in Table 2.

The purpose for choosing this organic material was to know the ability of both silicate and thermally treated samples toward adsorbing a polar substance like acetone. The higher ***SA*** by acetone adsorption could be due to the highly H-bonding of the studied samples with acetone molecules, since it is well-known that the reactivity of silica and alumina surfaces is strongly influenced by the degree of hydroxylation [18-21]. The adsorption of organic vapor to mineral oxide surfaces under ambient environmental conditions has been shown to follow three mechanisms (1) organic vapor adsorbed to the mineral oxide surface. The organic vapor can be physically adsorbed and or/ reacted with surface of aluminol or silanol group.(2) organic vapor adsorbed within or on the surface water film that adsorbed on the mineral surface.(3) organic vapor solvated into the adsorbed water layer (aquasi-liquid water layer). Mechanism (1) only occurs on surfaces that were not completely covered with water. With complete water layer coverage, mechanism (2) dominates for all the organics expect for polar molecules such as acetone and methanol or small organic acids. At very high water relative humilities (90-100 %), an increase of the adsorption was observed and it was speculated that this due to a change in the orientation of the water molecules that form the surface layer to which the organic adsorbs [20-21.].

The use of ***EGME*** by Carter et.al. for ***SA*** determination was for this material is more volatile, polar liquid with higher vapor pressure at room temperature than EG, and allows the evaporation to take place more quickly. Also, the samples are handled fewer timers using *EGEM*, and therefore, there are potentially fewer errors since the changes of introducing water vapor and other sources of errors are minimized. Another benefit to use ***EGME*** is that the maximum time to reach equilibrium is generally in the order of 16-24 hrs., depending on the type of silica, desiccant age, desiccator size, and other factors. This means that this test is completed in less time than using EG [7-8].

The ***SA*** values obtained by ***EGME*** adsorption for silicate and other samples of the present study were higher than other ***SA*** values as can be seen from Table2, which means that thermal treatment has caused an increase in the micro porous structure of the sample. As compared to some reported references, ***SA*** values of some silicates e.g Kaolinite, polygorskite and Hectorite determined by *EGME* adsorption were (26, 341 and 387 m^2/g) respectively[13] ,which means that our samples have more ability to retain ***EGEM*** than the reported mineral oxides. The amount of ***EGME*** retained depended on the type of the interlayer cations, thus, ***EGME*** retention inside the structure may be considered as a capillary infilling as well as surface absorption. The retention of *EGME* does not correlate with micro pore volume, however the incomplete dehydration (preheating at 250 ºC) allows for the partial ***EGME***-water substitution in micro pores and depends more on available mesopores surface area of micro pores infilling.

The ratio S_{A}/S_{EGME} reflects the microspore analysis, thus it means that pores are accessible for smaller molecules such as acetone and *EGME*. This ratio was lower in ***MB*** and ***PNP*** as compared with acetone which means that the sample is micro porous (contains narrow micro pores). This is for adsorption from vapor phase took place more easier than solution phase (vapor penetrate easily into pores), while in solution diffusion becomes more difficult because of aggregation since organic dyestuffs are adsorbed in ionic micelles from the aqueous solution[1].

By arranging the ***SA*** values calculated by various adsorbates of different sizes, it could be seen that ***SA*** values decreased in the order: $\mathbf{SA_{EGME}>SA_{Acetone}>SA_{PNP}>SA_{MB}}$,this may lead us to conclude that silicate of the present study is highly micro porous due to their higher SA by *EGME* adsorption and acetone in comparison to those obtained by solution adsorption may be because of the former reason.

X-ray diffraction analysis:

The studied sample which locally known as "Ninavite' consists mainly of three silica polymorphous (quartz, opal-CT and opal-A). Quartz gives a strong X-ray diffraction pattern as shown in Figures (4 and 5), the strongest reflection of d-spacing is at 3.343 A°. In this study, quartz is used as an internal standard for the d-spacing measurement of opal-CT. The latter has ***XRD*** pattern consisting of three broad reflections with d-spacing of 4.26, 4.06 and 2.485 A° as Figure 5. It forms with opal-A meta stable variety of hydrous silica which could be inverted at temperature above 600 C° which is the high temperature polymorphs concomitant with a decrease in specific surface area. The two diffractgrams are identical and therefore there was no effect of heat on mineral phases.

Conclusions

1- The present study disclosed the possibility of making use of some naturally available adsorbent such as our silica for purifying waste water from some organic pollutants.

2- Also ,the study indicated the high porosity of our silica which detected from the highly surface area of both acetone and EGME adsorption.

3- Thermal treatment of the used silicate showed a clear enhancement in the surface area

4- On the other hand, the results showed high porosity of our silica, and thermal treatment causes a clear enhancement in the surface area which in turn improved adsorption ability in both vapor and solution phase.

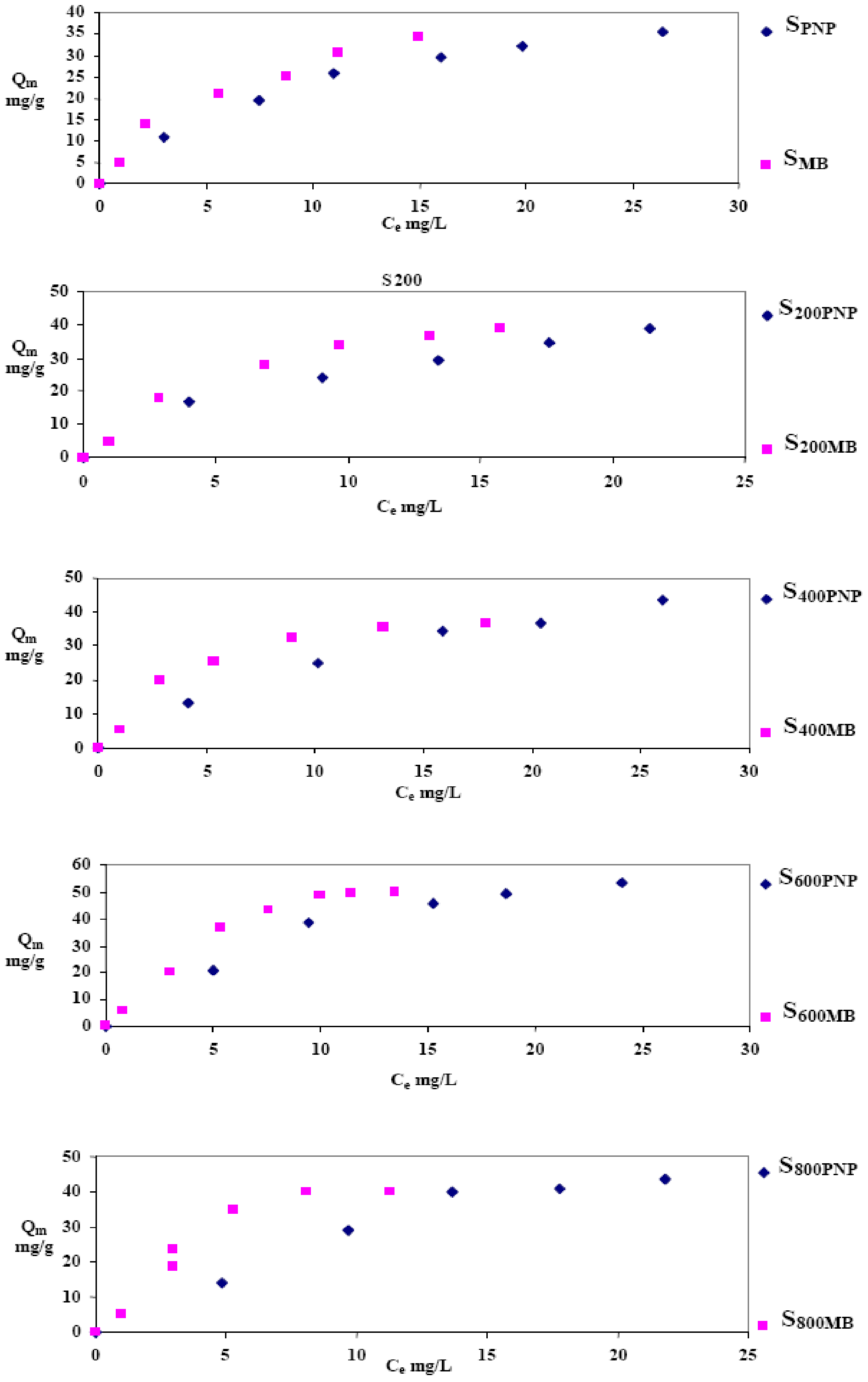


Figure 3. .dsorption isotherms of PNP and MB of the studied samples at 298 K.

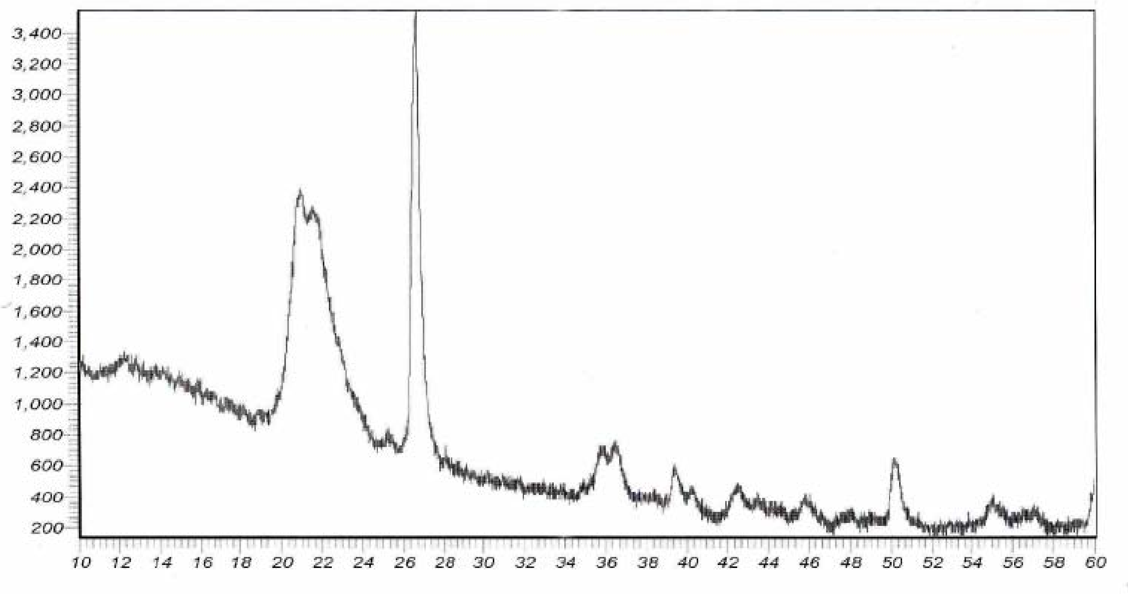


Figure 4 X–ray diffractogrom of the studied porcellanite.

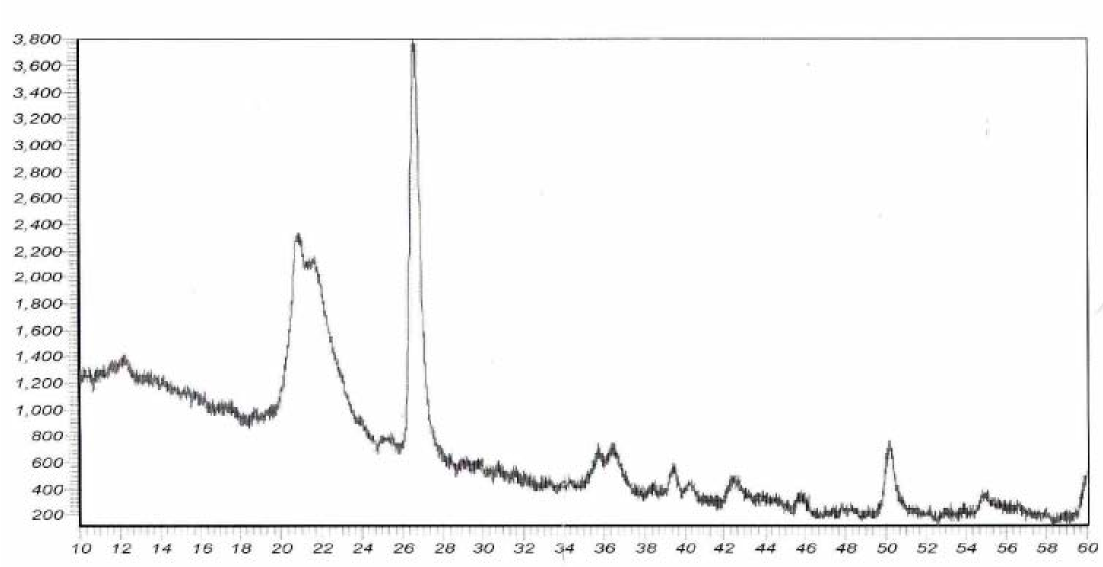


Figure 5 X–ray diffractogrom of S_{600} sample.

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