Determination The Effect of ZnO on Iraqi Bentonite Surface Properties

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Abstract:

Bentonite is widely used in industrial applications. The present study reports the effect of adding different weights of ZnO to the Iraqi bentonite, on surface area, pore volume and real density. These surface properties were evaluated for pure and modified bentonite. The modification was made by adding different ZnO weights such as; (0.5%, 1%, 5%, 10%). The effect of heat exposing for all modified clay samples at 500 ^{o}C have been also evaluated. The results show that the addition of 0.5% ZnO leads to increase the surface area percentage about 36%, increase pore volume percentage about 5.48% and increase the real density percentage about 27.116%. When the samples exposed to 500 ^{o}C, their surface area and pore volumes have been decreased and the real density increased in compared with non-heat exposed samples.

Key words: Bentonite, Modified clay, Surface area, Pore volume, Real density.

Introduction:

Clays are hydrous aluminosilicates composed of mixtures of fines-grained clay minerals, crystals of other minerals and metal oxides. Clays play an important role in the environment by taking up cations and anions through adsorption or ion exchange. They belong to low cost sorbendts[1], as the cost is an important parameter. The good adsorption ability comes from their negative charge which can be neutralized by adsorption of positively charged cations.

Clays obtaining montmorillonite are referred to bentonite which belongs to the 2:1 clay family composed of two tetrahedrally coordinated sheet of silicon surrounding and an octahedrally coordinated sheet of aluminum ions. Clay can be modified to improve its sorption ability[2,3]; one of the methods is the use of magnetic modification in which, e.g., bentonite coated with iron can be obtained[4].

Surface area and pore sizes play an important role in physical adsorption, chemisorption and catalysis[5]. Diffusion into narrow pores may become the rate-determining step for any of these processes. The sizes of the pores in any solid can influence the order and the energy of activation of any reaction that takes place on the surface of the solid, it may also determine the extent to which a porous solid can build up temperature and pressure gradients in the course of the reaction. The suitability of an adsorbent for certain specific applications may be determined by the pore structure and pore-size distribution[6-8]. Surface area is an attributed that is used by catalyst manufacturers and users to monitor the activity and stability of catalysts.

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The aim of this work was to modify Iraqi bentonite clay by adding ZnO, and study the best addition which increases the surface area, pore size and real density by using the multipoint Brunaner, Emmett and teller (BET) method to measure total surface area[9]. The data from multipoint determination are used to calculate the matrix surface area by use of the t-plot method of Lippens and deboers[10,11].

Material and Methods:

Modified bentonite samples were prepared from a solutions containing a mixture of ZnO + bentonite and distilled water, treated by stirring method for 24 hours at 25 ^{o}C, different ZnO weight were used (0.05, 0.1, 0.5, 1) grams with 10g of Iraqi bentonite which supplied from (Iraqi Geologecial scanning office), 75 μm practical size were introduced into four flasks, into which 50 ml of distilled water were already present.

All experiments were carried out in 250 ml round bottom flasks at a constant temperature of 25 OC using a rotary shaker (100 rpm), the suspension was then filtered and the modified clay dried in oven with 70 OC until it become powder. For characterization of the surface and pore properties of the prepared modified clays, nitrogen adsorption experiments were carried out at 77K with an Thermofinnagn – Thermoscientific apparatus model M1 96005 BET, N_2 and for pore volume Autolab / Quantacchrom ASTM D – 4164, D – U781 was used. The real density of the four modified clays were carried out with picnometer PMI – USA PYP – G 100 A_1.

The specific surface area S_{BET} was calculated from the adsorption isotherms according to the BET method in a relative pressure range 0.03-0.2 P/P_o. The value of the total pore volum Va was determined from the maximum adsorption at a relative pressure 0.99 P/P_o.

Result and discussion:

The concept of the BET theory is an extension of the Langmuir theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is expressed by (1):

$$\frac{1}{\upsilon[(\frac{P}{P_o})-1]} = \frac{c-1}{\upsilon_m c}\left(\frac{P}{P_o}\right) + \frac{1}{\upsilon_m c} \quad \text{.............(1)}$$

P and P_o are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, υ is the adsorbed gas quantity (for example, in volume units), and υ_m is the monolayer adsorbed gas quantity. C is the BET constant, which is expressed by (2):

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right) \ldots\ldots\ldots\ldots(2)$$

E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction.

Equation (1) is an adsorption isotherm and can be plotted a straight line with 1/ υ [(P/ P_o) -1] on the y-axis and φ = P/P_o on the x-axis according to experimental results. This plot is called a BET plot. The linear relationship of this equation is maintained only in the range of 0.05< P/P_o< o.35. The value of the slop of the relation between $1/\upsilon \cdot \frac{\varphi}{1-\varphi}$ against φ[12] and y-intercept of the line are used to calculate the monolayer adsorbed gas quantity υ_m and the BET constant c.

The results obtained of these parameters are summarized in Table 1

Table (1): The values of BET surface area total pore volume and real density for pure bentonite and four Iraqi modified bentonite.

Physical properties	P-B	1-B	2-B	3-B	4-B
	Pure-B	0.05 / g ZnO	0.1 / g ZnO	0.5 / g ZnO	1 / g ZnO
Surface Area (m^2/g)	64.1748	87.2993	86.5056	79.073	69.1265
Pore Volume cm^3/g	0.1313	0.1385	0.1376	0.1133	0.1152
Real density g/cm^3	1.8978	2.4124	2.281	2.5433	3.179

It is clear that znO led to increase the surface area of the Iraqi bentonite specially when it used in a low amount (0.05g) so it followed the order:

P-B < 4-B < 3-B < 2-B < 1-B

While the order of the pore volume has been as:

4-B < 3-B <P-B <2-B < 1-B

And the sequence for the real density takes the following order:

P-B < 2-B < 1-B < 3-B < 4-B

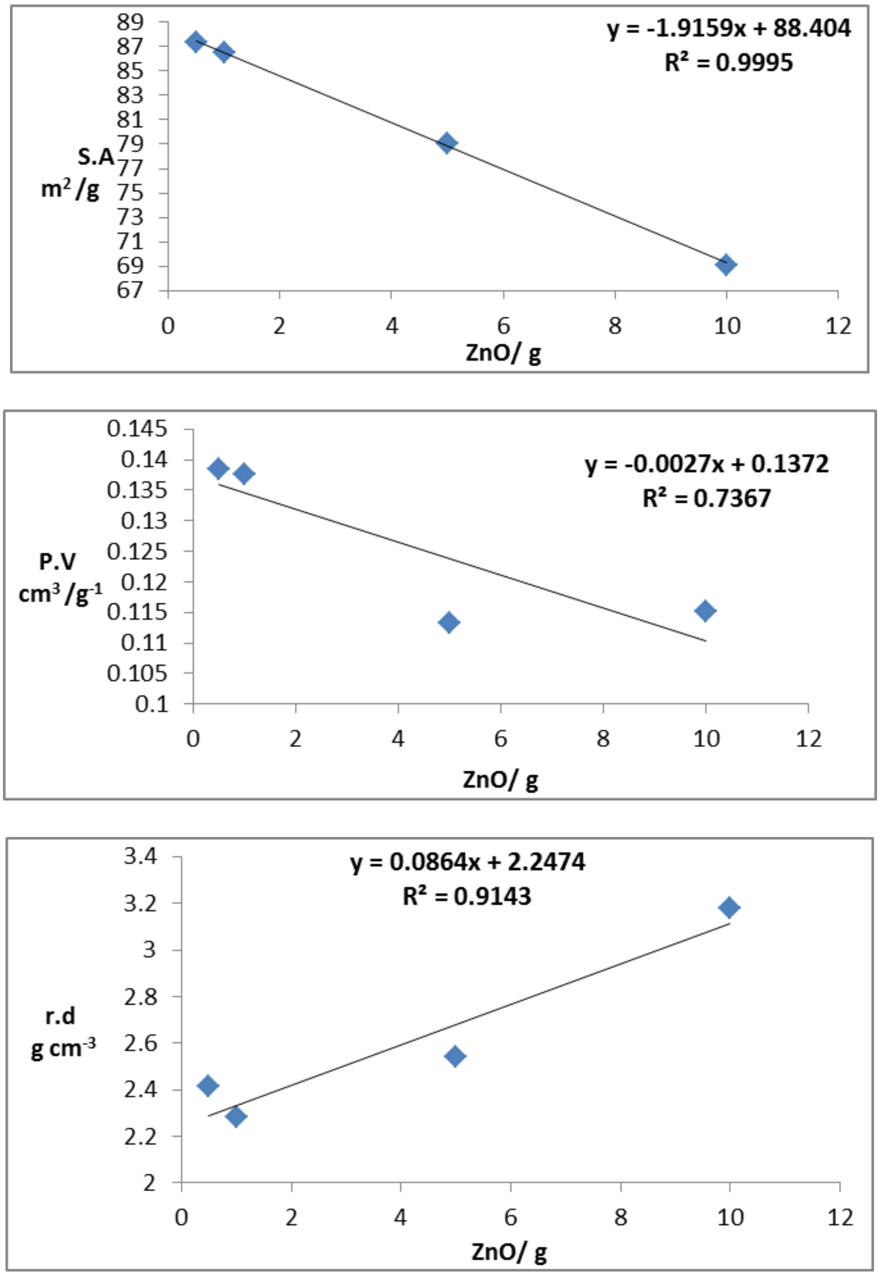
That means using 0.05g of ZnO leads to the best increasing in surface area and pore volume, we suggest that nano particles appear while the higher concentration of ZnO leads to decrease the surface area because it full's the pores but lead to decreasing the real density.

The percentage of the increase are represented in the following Table (2).

Table (2): Surface area, Pore volume and Real density percentage for the modified clays

Physical properties	1-B	2-B	3-B	4-B
Surface Area % (S.A)	36.034	34.797	23.215	7.716
Pore Volume % (P.V)	5.484	4.798	- 13.709	- 12.262
Real density % (r.d)	27.116	20.192	34.013	67.519

The variation of the surface properties with the ZnO addition were represented in Fig 3:



Fig(3): Variation of (a) surface area, (b) pore volume and (c) real density with ZnO additions

The varation of surface area with ZnO addition gives a linear relationship with R^2 0.9995 and intercept 88.404 m^2/g which means that using nano percentage of ZnO leads to increase surface area from 64.1748 to about 88.404 m^2/g or leads to increase the surface area to about 37.755% so using 0.05g of ZnO leads to about the highest surface area percentage increasing 36.034%.

The effect of exposing the four modified clays to 500 ^oC on the surface properties were also evaluated and Table 3 shows the decreasing of surface area and pore volume for four samples and shows the increasing of the real density.

Table(3): Surface area, Pore volume and Real density for the modified clays after exposing to 500 °C.

Physical properties	1-B	2-B	3-B	4-B
(S.A) / m^2g^{-1}	49.5508	44.4904	52.139	34.99
(P.V) / cm^3g^{-1}	0.1077	0.09532	0.1105	0.077
(r.d) / g cm^{-3}	3.2681	3.3854	4.7033	5.9504

The surface area and pore volume after exposed to 500 °C followed the sequence:
3-B > 1-B >2-B > 4-B
The real density after being exposed to 500 °C followed the sequence:
4-B >3-B >2-B >1-B

All surface properties for exposed samples to 500 °C decrease than that surface properties for unexposed samples and for pure bentonite.

Fig.4 shows the effect of adding ZnO to modified bentoniteafter exposed to 500 °C for 6 hours.

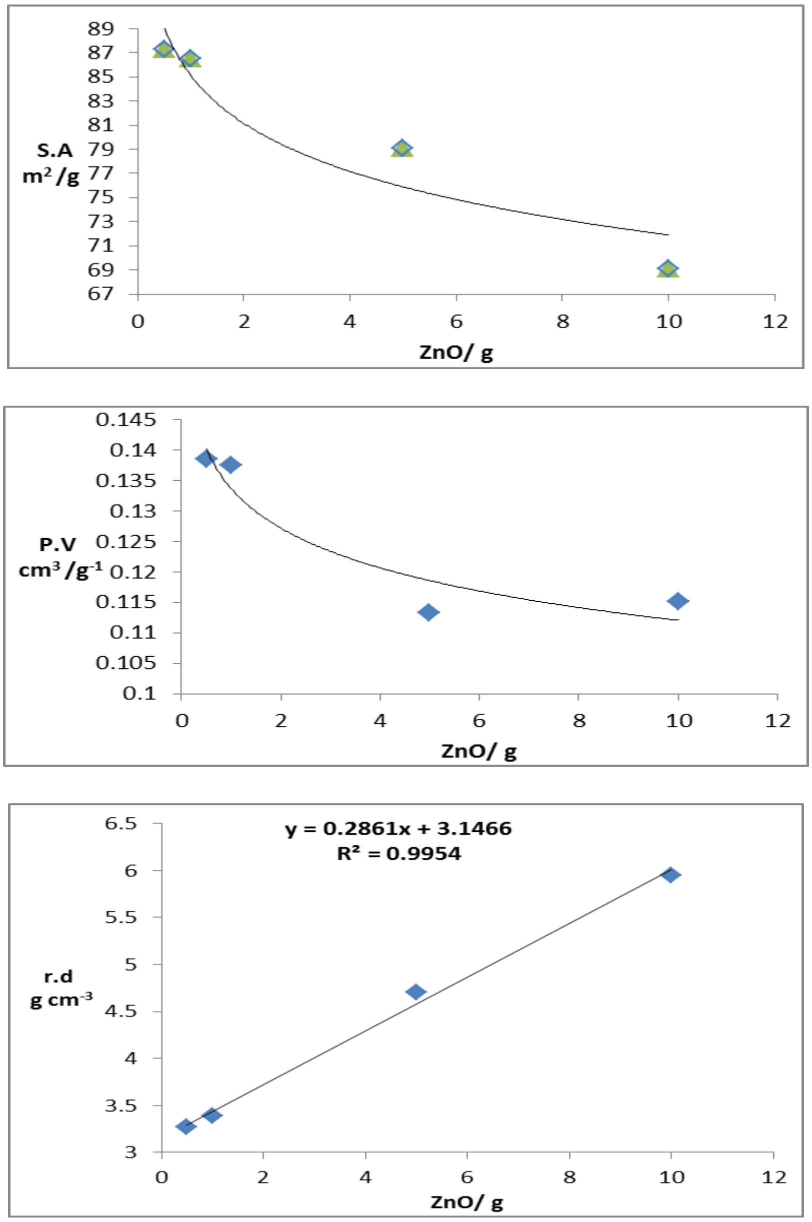


Fig (4) Variation of (a) surface area, (b) pore volume and (c) real density with ZnO additions for modified exposed to 500 °C

It clear that the relationship between real density and ZnO quantity was linear with R^2= 0.9954 while the two other relation were non-linear.

Conclusion:

Bentonite clay can be modified to increase its surface area and pore volumes by adding ZnO in the quantity bellow 0.05 g / 10 g bentonite to increased surface area about 37% and to increase pore volume to about more than 5.5%. heat exposing was useless for modified Bentonite clay.

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تعيين تأثير اوكسيد الخارصين على خواص سطح البنتوبايت العراقي

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الخلاصة:

طين البنتونايت له استخدامات واسعة في مجال التطبيقات الصناعية، في هذه الدراسة تمت متابعة تأثير اضافة أوزان مختلفة من أوكسيد الزنك لـ 10 غم من البنتونايت العراقي، على صفاته السطحية مثل المساحة السطحية، حجم المسام والكثافة الحقيقية للأطيان. تم تقدير الخواص السطحية للطين النقي وطين البنتونايت المحسن (باضافة أوزان مختلفة من أوكسيد الزنك g (0.05 ,0.1 ,0.5 ,1) الى 10 غم من البنتونايت في 50 مل من الماء المقطر كمحلول عالق. تم تقدير تأثير تعريض نماذج الطين المحسنة في درجة حرارة 500 مئوي. بينت النتائج ان اضافة 0.05 غم من أوكسيد الزنك تؤدي الى زيادة المساحة السطحية بنسبة مئوية حالي 36%، وزيادة حجم المسام بنسبة 5.48% وزيادة نسبة الكثافة الحقيقية بـ 27.116%. تعريض النماذج لدرجة حرارة 500 ^{o}Cأدى الى تقليل المساحة السطحية وحجم المسام وزيادة الكثافة النسبية مقارنة بالنماذج غير المعرضة للحرارة.