

Adsorptive removal of phosphate from aqueous solutions using raw and calcinated dolomite

S. Karaca^{a,*}, A. Gürses^b, M. Ejder^a, M. Açıkyıldız^b

^a Department of Chemistry, Atatürk University, Fen-Edebiyat Fakültesi, 25240 Erzurum, Turkey

^b Department of Chemistry, Atatürk University, K.K. Eğitim Fakültesi, 25240 Erzurum, Turkey

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Abstract

This study explored the feasibility of utilizing raw and calcinated dolomite under CO₂ atmosphere for phosphate removal in laboratory experiments. The experimental work emphasized the evaluation of phosphate adsorption characteristics of this adsorbent material. Studies were conducted to delineate the effect of contact time, initial phosphate concentration, temperature, pH, stirring speed, adsorbent dose and calcination temperature. Phosphate removal decreased with increasing temperature and slightly increased with increasing of pH. The observed decrease in the adsorption capacity with increase of the temperature from 20 to 40 and to 60 °C indicates that the low temperatures favor the phosphate removal by adsorption onto dolomite. Phosphate removal was seen to decrease with increasing calcination temperature due to the structural changes occurring in the structure and pore size distribution of dolomite samples during calcination. The experimental data obtained were applied to the Freundlich, Langmuir, BET, Halsey, Harkins–Jura, Smith and Henderson isotherm equations to test the fit of these equations to raw and calcinated dolomite samples. By considering the experimental results and adsorption models applied in this study, it can be concluded that adsorption of phosphate occurs predominantly through physical interactions, and the dolomite sample has a heteroporous structure. The large values of the constants for Henderson equation and the high value of y_m obtained from BET equation indicate the microporous structure is more stable in raw and calcinated dolomite samples.

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1. Introduction

Phosphate is recognized as being one of the resources that will be lost in near future [1]. A large amount of used phosphate finally reaches water environment as diluted waste, which often leads to pollution of the water environment. It is of value to collect the finally disposed phosphates from effluents and drain water before further dispersion and dilution of them in the water environment. Many techniques have been proposed for the removal of phosphate from wastewater. Coagulation–precipitation and biological methods are widely accepted methods of phosphate removal at industrial level. Extensive research has also been carried out to produce simplification of maintenance, stable running and removal efficiency. Among these researches, many researchers have pro-

moted development of adsorbents with high selectivity and removal capacity for phosphate [1–6]. Recent recognition of the risk of very dilute contaminants in water makes it important to produce a new kind of adsorbents and/or coagulants to avoid any risk that may be produced such as contamination by the agents through their dissolution [7,8].

The objective of this work was to study the feasibility of using raw and calcinated dolomite under CO₂ atmosphere as an adsorbent for phosphate removal from wastewater. Dolomite is a common sedimentary rock-forming mineral that can be found in sedimentary beds several hundred feet thick, it is also found in metamorphic marbles, hydrothermal veins and replacement deposits. Dolomite is both a mineral and a rock. The Dolomite Group is composed of minerals with an unusual trigonal bar 3 symmetry. The general formula of this group is AB(CO₃)₂, where A can be calcium, barium and/or strontium and the B can be iron, magnesium, zinc and/or manganese. The amount of calcium and magnesium in most specimens is equal, but occasionally one element may have a slightly greater presence than

* Corresponding author. Tel.: +90 442 231 4435; fax: +90 442 236 0948.
E-mail address: skaraca@atauni.edu.tr (S. Karaca).

the other. Small amounts of iron and manganese are sometimes also present [9,10].

The adsorption characteristics of this material for phosphate removal from aqueous solutions were evaluated in small-scale experiments. The scope included the effect of initial phosphate concentration, adsorption temperature, pH, stirring speed, adsorbent dosage and calcination temperature on the adsorption of phosphate. The adsorption isotherms were evaluated in batch jar tests by using orthophosphate solutions. Such work could contribute to understanding the phosphate removal process using dolomite.

2. Materials and methods

The dolomite sample used in this study was supplied from the Erzurum region, in Turkey. The sample was air-dried and then sieved to give a $-180/+425$ m size fraction using ASTM Standard sieves. The chemical composition of the dolomite sample was estimated by comparing X-ray diffraction diagrams of the reference dolomite and the sample used in this study, and these are given in Fig. 1. As seen in Fig. 1, X-ray diffraction diagrams are almost the same, indicating that the sample dolomite used is the same as the reference dolomite. The chemical composition of the reference dolomite is 21.7% Ca, 13.2% Mg, 13.0% C and 52.1% O. Then, by dissolving the sample with HCl, it was found that the sample contained dolomite at 99.5%. Phosphate was removed by using dolomite from synthetic wastewater in this study. All chemicals used in this study were obtained from Merck.

Adsorption experiments were carried out in 100-mL glass-stoppered round-bottom flasks immersed in a thermostatic shaker bath. For this, 0.2 g of the raw and calcinated dolomite sample was mixed with 100 mL of the aqueous solutions of the various initial concentrations (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/L) of phosphate. The dolomite samples were previously calcinated in muffle furnace at the temperature of 350, 450 and 700 °C for 10 min and under CO₂ atmosphere.

The standard phosphate solutions used in the experiments were prepared from anhydrous KH₂PO₄. The flasks with their contents were then shaken for the different adsorption times at 20, 40 and 60 °C and natural pH. The effect of pH was investigated at 20 °C. pH adjustments have been done using solutions of concentrated HCl and NaOH. In the experiments, the stirring speed was kept constant at 90 rpm (except for the experiments in which the effect of stirring speed are examined). At the end of adsorption period, the supernatant was centrifuged for 2 min at 3750 min⁻¹. The concentration of phosphate in the supernatant solution after and before adsorption was measured according to the stannous chloride method [11]. The measurements were made at the wavelength = 690 nm, which corresponds to maximum absorbance. The adsorbed amount of phosphate was calculated from the concentrations in solution before and after adsorption. Blanks containing no phosphate were used for each series of experiments. The specific surface area of dolomite was measured using the BET N₂ method and is found to be 0.14 m²/g.

3. Results and discussion

3.1. Effect of temperature

To investigate the effect of adsorption temperature on the phosphate adsorption onto the dolomite surface, experiments were carried out with varying initial concentrations of phosphate from 10 to 100 mg/L at different agitation times (10, 15, 30 and 60 min), at three different temperatures (20, 40 and 60 °C) and at a constant stirring speed of 90 rpm. The results are given in Figs. 2 and 3. As can be seen from these figures, the adsorption of phosphate onto the surface of dolomite taken place quickly at high initial phosphate concentrations (after 50 mg/L) until first 15 min while the time required to reach adsorption equilibrium raised until 30 min at low initial phosphate concentrations, at all of studied temperatures. The variation in the adsorption equilibrium time is significantly different at low initial phosphate concentrations at all of temperatures. But, the time of 15 min is sufficient at high initial phosphate concentrations. After these

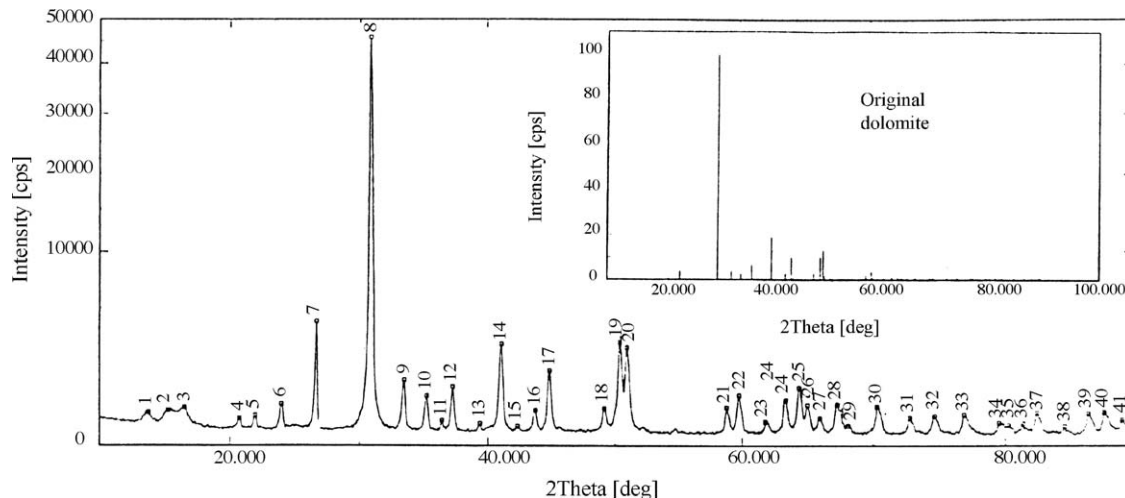


Fig. 1. X-ray diffraction diagrams for the reference dolomite sample and the sample used in this study.

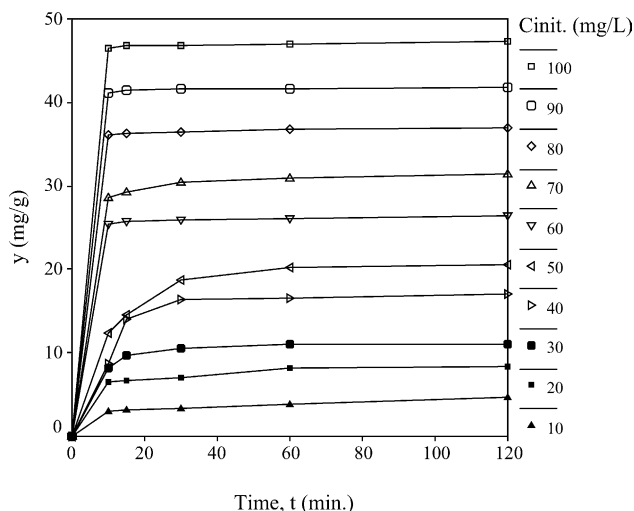


Fig. 2. The variation of adsorption capacity with adsorption time at various initial phosphate concentrations (solid–liquid ratio 0.2 g/100 mL, stirring speed 90 rpm, natural pH \approx 3.54 and temperature 20 °C).

adsorption times, the adsorption rate exhibits the tendency to be constant. Therefore, it can be said that in order to reach adsorption equilibrium, the adsorption times of about 15 and 30 min are sufficient for high and low concentrations, respectively. The observed relative decrease in equilibrium time at high initial phosphate concentrations can be attributed to the difference of phosphate concentrations in the solid and bulk phase (concentration gradient). It is known that diffusion rates increase as the concentration gradient increases. Adsorption capacity increased with increasing initial phosphate concentration. The relative shorter equilibrium adsorption time in this study can be attributed to the intensive physical interactions between phosphate ions and the surface of dolomite. It has been reported that the time required for reaching adsorption equilibrium is short for the adsorption processes in which physical interactions are

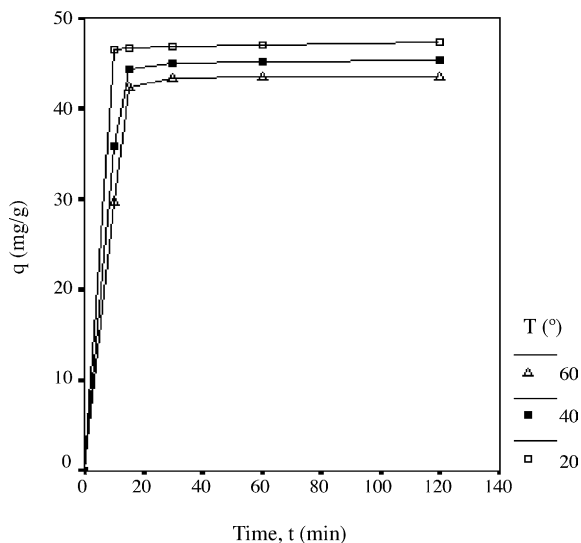


Fig. 3. The variation of adsorption capacity with adsorption time at various adsorption temperatures (solid–liquid ratio 0.2 g/100 mL, stirring speed 90 rpm, natural pH \approx 3.54 and initial phosphate concentration 100 mg/L).

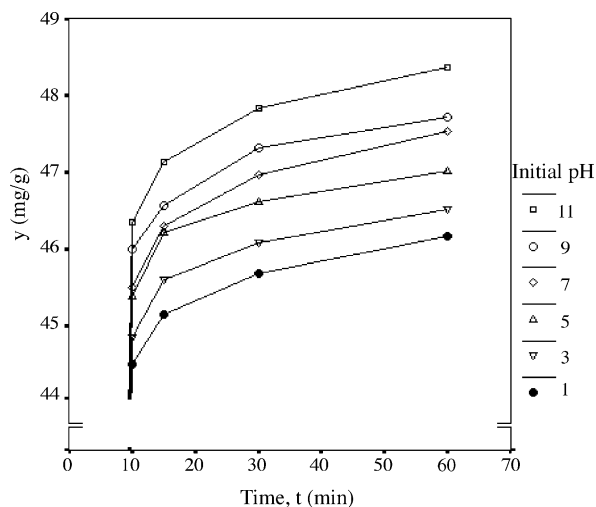


Fig. 4. The variation of the amount adsorbed with adsorption time at various initial suspension pHs (solid–liquid ratio 0.2 g/100 mL, stirring speed 90 rpm, initial phosphate concentration 100 mg/L and adsorption temperature 20 °C).

predominant [12–14]. The observed decrease in the adsorption capacity with an increase of the temperature from 20 to 40 and to 60 °C indicates that the low temperatures favor phosphate removal by adsorption onto dolomite. This may be due to a tendency for the phosphate ions to escape from the solid phase to the bulk phase with an increase in the temperature of the solution [15,16]. This effect suggests that an explanation of the adsorption mechanism associated with the removal of phosphate onto dolomite involves a physical process in this case, in which adsorption arises from the electrostatic interactions, which is usually associated with low adsorption heat.

3.2. Effect of pH

To study the influence of pH on the adsorption capacity of dolomite for phosphate, experiments were performed at 20 °C, for several contact times, using various initial solution pH values, changing from 1 to 11 (Fig. 4).

The pH dependency of phosphate removal is both related to the dissolution of Ca^{2+} ions from adsorbent and to the polyprotic nature of phosphate. Previous workers reported that Ca^{2+} concentrations in the solution decrease with increasing initial pH for different phosphate concentrations and they are also suggested that the phosphate removal by fixation with Mg^{2+} ions was not accomplished or it was low. The formation of calcium phosphate precipitates in amorphous form can be expected [17]. Moreover, when the pH of the solution decreases, the positively charged surface sites formed on the adsorbent favor the adsorption of phosphate due to the electrostatic attraction. As the pH of solution is increased, the concentration of OH^- in solution, which competes with the PO_4^{3-} species, becomes higher.

The highly negatively charged adsorbent surface sites do not favor the adsorption of oxianion due to the electrostatic repulsion [17,18].

In this study, the phosphate removal was not significantly changed with increasing of solution pH. This may be explained

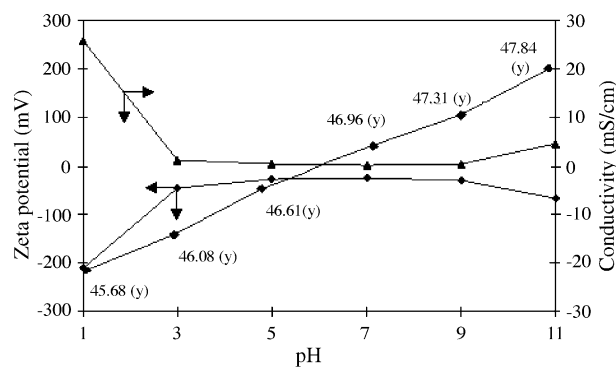


Fig. 5. The variation of the values of zeta potential, values of conductivity and the amounts adsorbed with initial suspension pH (solid–liquid ratio 0.2 g/100 mL, stirring speed 90 rpm, initial phosphate concentration 100 mg/L and temperature 20 °C, for 60 min, y: adsorption capacity, mg/g).

by considering such competing effects as a decrease in the dissolved Ca^{2+} concentrations and an increase of PO_4^{3-} species from hydrolysis products of phosphate and OH^- concentration in solution with increasing pH.

The values of zeta potential of the particles were measured by using a microelectrophoresis cell (Zeta meter 3.0+). Fig. 5 shows the variation of both the values of zeta potential and electrical conductivity with suspension pH, together with the adsorption capacities at studied each pH. As seen from the figure, the highest negative zeta potential was observed at pH 1, where the electrical conductivity was the highest and the lowest adsorption capacity are obtained for pH 1. At this pH, other species of phosphate such as HPO_4^{2-} , H_2PO_4^- and H_3PO_4 are prevalent and HCO_3^- ions decompose from the dolomite surface. The most high value of electrical conductivity is supported this probability. Also, it may be said that the high negative charge on the dolomite surface arisen from HCO_3^- and other hydrolysis products of phosphate (less in according to the case of PO_4^{3-}), which are adsorbed onto dolomite surface through physical, such as ion–dipole and/or dipole–dipole interactions. When the suspension pH is reached to 3, both the value of zeta potential and the value of electrical conductivity is rapidly approached to zero. Neither zeta potential nor electrical conductivity did significantly change in the range of pH 3–9. The values of zeta potential of particles are slightly increased as positive, while the value of electrical conductivity is decreased near zero in this range. At pH 11, both of the value of zeta potential and electrical conductivity are increased again.

3.3. Effect of stirring speed

Experiments were conducted to investigate the effect of stirring speed on the phosphate adsorption onto the dolomite for initial phosphate concentration of 100 mg/mL and different adsorption times, at 20 °C, stirring speeds in the range of 90–150 rpm. The results are given in Fig. 6. As can be seen from this figure, with increasing stirring speed the adsorption capacity of phosphate did not change. This indicates that the diffusion of the phosphate ion from the solution to the surface of the adsorbent and into the pores occurs easily and quickly.

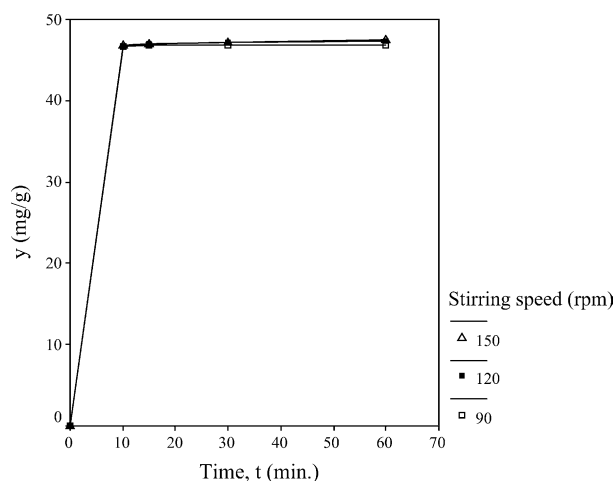


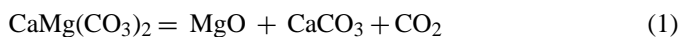
Fig. 6. The variation of the adsorption capacity with adsorption time at various stirring speeds (solid–liquid ratio 0.2 g/100 mL, natural pH \approx 3.54 and initial phosphate concentration 100 mg/L for 20 °C).

3.4. Effect of adsorbent dose

To investigate the effect of adsorbent dose on the phosphate adsorption onto the dolomite surface, experiments were carried out with initial phosphate concentration of 100 mg/L and varying adsorbent dose at 20 °C and at a constant stirring speed of 90 rpm for 60 min. The results show that the percent removal increased with increasing adsorbent dose due to the increase in the total available surface area of the adsorbent particles.

3.5. Effect of calcination on the phosphate adsorption

The results of the effect of the calcination on the surface topography of dolomite and the adsorption capacity of phosphate were presented in Figs. 7 and 8, respectively. Thermal decomposition of dolomite occurs via a system involving a number of reactions still being under discussion in the literature [19]. When it takes place in air or in the presence of CO_2 , it occurs as a two-step process, usually written as [20]:



There is a discrepancy in the literature about the limiting partial pressure of CO_2 that switches the course of dolomite decomposition [21]. Moreover, the precise mechanism of this process is not established yet. According to Hashimoto et al. [22], the two step decomposition of dolomite may undergo through either dissociation into magnesium and calcium carbonates, followed by the decomposition of magnesium carbonate, or the decay of the dolomite structure into the mixture of oxides and then secondary recarbonation of calcium oxide to calcium carbonate. Apart from these, when decomposition of dolomite is stopped after the first step, the product is a solid consisting of a rigid, porous calcite and the fine powdered magnesium oxide. The porosity and surface properties of such obtained solid, a so-called “dolomitic sorbent”, depend on the conditions of thermal treatment. Obviously, the gas–solid reactions are accompanied

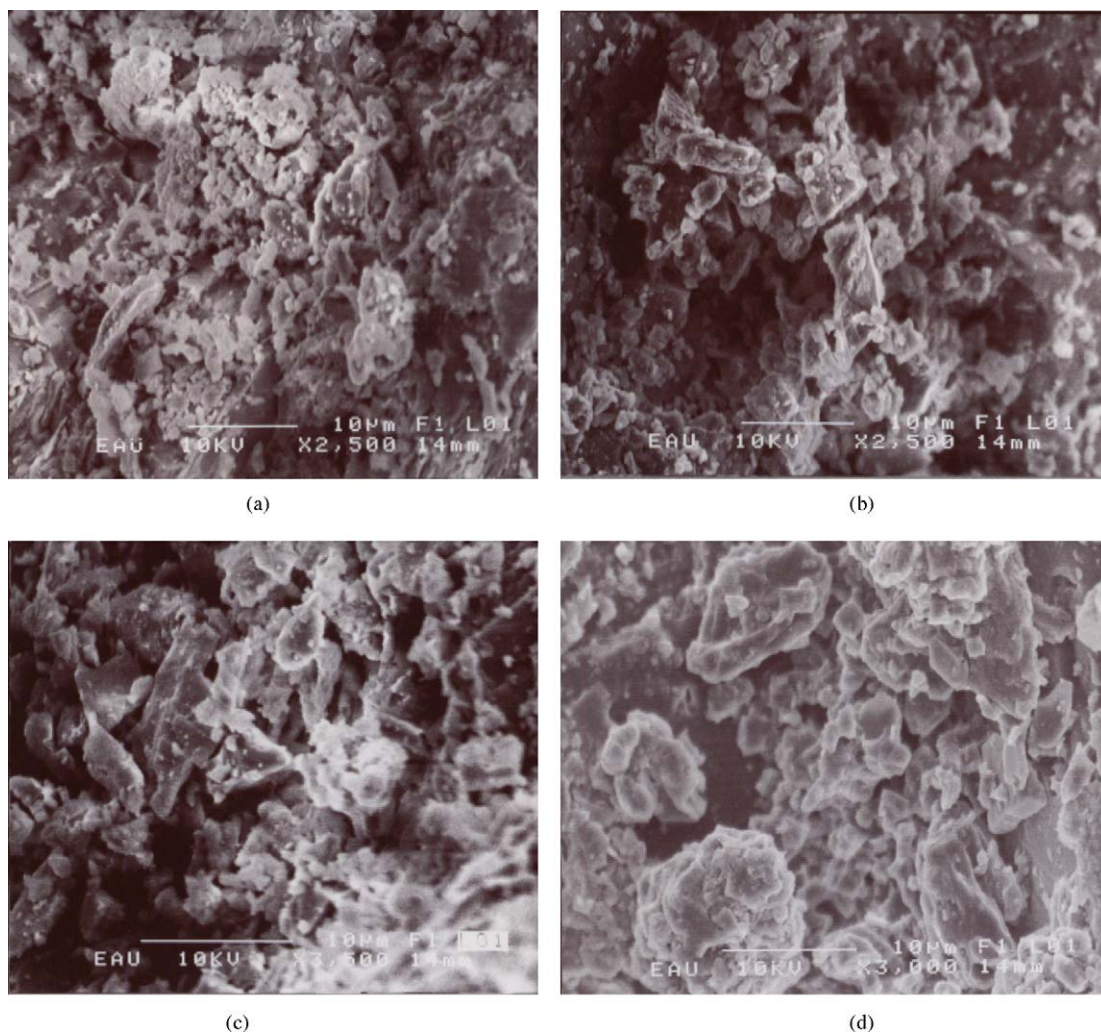


Fig. 7. SEM images of the raw dolomite and the calcinated samples under CO_2 atmosphere at several temperatures: (a) raw, (b) 350°C , (c) 450°C and (d) 700°C .

by structural changes within the solid product which are not only a direct result of the chemical change in the solid but also the processes as sintering, cracking, swelling, etc. [23]. Carbon dioxide accumulation has the major role in the development of

a porous structure of dolomitic sorbents. The diffusion rate of carbon dioxide outside the sample bed is negligible in pure CO_2 atmosphere. The structural changes within a new solid phase of calcite, usually promoted by the high concentration of CO_2 , such as sintering or shrinkage, lead to the increase of a solid density, decrease of pore numbers and specific surface area [21].

In our work, to estimate the porosity changes that occur during the thermal treatment of dolomite under CO_2 atmosphere both the phosphate adsorption measurements and SEM images for raw dolomite and the samples calcinated at various calcination temperatures were applied. The SEM images of the samples and results for adsorption measurements are given in Figs. 7 and 8, respectively. Fig. 7 shows that the pores for sample calcinated at 350°C are relatively more open than that of raw sample. However, calcinations at the higher temperatures have caused to covering of the pores and so significantly changing of the surface topography of the samples. As seen from Fig. 8, the adsorbed amounts of phosphate on calcinated dolomite sample under CO_2 atmosphere at 350°C are also slightly higher in comparison with those on the raw dolomite. But, beyond the temperature 350°C , the adsorption capacity is slightly reduced in calcinated dolomite samples under CO_2 atmosphere 450 and

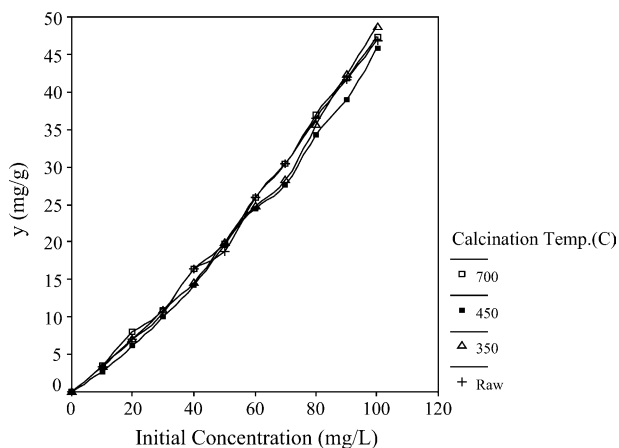


Fig. 8. The variation of adsorption capacity with initial phosphate concentration at various calcination temperatures (solid–liquid ratio 0.2 g/100 mL, natural $\text{pH} \approx 3.54$, stirring speed 90 rpm and adsorption temperature 20°C , for 60 min).

700 °C. The observed decrease in adsorption capacities with increasing calcination temperature can be attributed to the structural changes occurring in the structure and pore size distribution of dolomite samples during calcination [21].

3.6. Adsorption isotherms

In order to determine the mechanism of phosphate adsorption on the raw and calcinated dolomite sample at 350 °C the experimental data were applied to the Freundlich, Langmuir, BET, Halsey, Harkins–Jura, Smith and Henderson isotherm equations. The constant parameters of the equations for this system were calculated by regression using the linear form of the isotherm equations and SPSS 10.0 software. The results are given in Table 1, together with the isotherm equations.

The isotherms belonging to the phosphate adsorption on the raw and calcinated dolomite samples under CO₂ atmosphere at 350 °C are given in Fig. 9. As seen from this figure, the

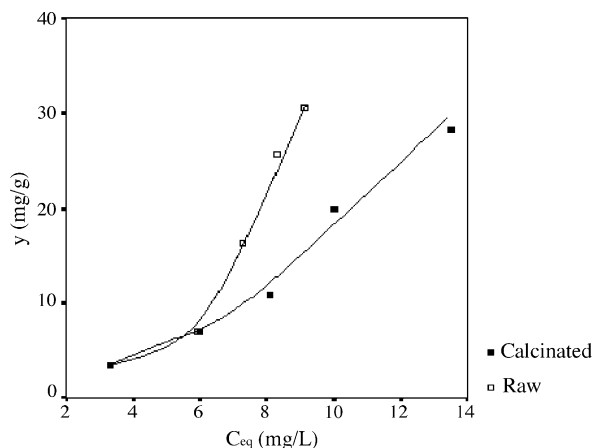


Fig. 9. The adsorption isotherms of the phosphate on raw and calcinated dolomite under CO₂ atmosphere at 350 °C (adsorption temperature 20 °C for 60 min).

Table 1
Applicability of isotherm equations to phosphate adsorption data at 20 °C of raw and calcinated dolomite samples under CO₂ atmosphere at 350 °C and their constant parameters

Isotherm equations	Sample	Constant parameter	R ²
Freundlich, $\ln y = \ln k + n \ln C$	Raw	$n = 2.15$ $k = 0.257$	0.9935
	Calcinated	$n = 1.52$ $k = 0.534$	0.9833
Langmuir, $C/y = 1/ky_m + (1/y_m)C$	Raw	–	–
	Calcinated	–	–
BET, $C/y(1 - C) = 1/(y_mk) + [(k - 1)/(y_mk)]C$	Raw	$y_m = 805.94$ $k = 0.911$	0.9882
	Calcinated	$y_m = 914.20$ $k = 0.957$	0.9984
Halsey, $\ln y = [(1/n) \ln k] - (1/n) \ln[\ln(1/C)]$	Raw	$n = 0.09$ $k = 6.340$	0.9995
	Calcinated	$n = 0.13$ $k = 6.689$	0.9860
Harkins–Jura, $1/y^2 = (B/A) - (1/A) \log C$	Raw	$A = 4.50$ $B = -0.986$	0.9737
	Calcinated	$A = 5.59$ $B = -0.966$	0.9350
Smith, $y = W_b - W \ln(1 - C)$	Raw	$W_b = -12.57$ $W = 4489.06$	0.9479
	Calcinated	$W_b = -6.23$ $W = 2536.47$	0.9844
Henderson, $\ln[-\ln(1 - C)] = \ln k + n \ln y$	Raw	$n = 2.14$ $k = 684.105$	0.9936
	Calcinated	$n = 1.54$ $k = 209.104$	0.9785

y is the adsorption capacity of phosphate (mg/g); y_m is the monolayer adsorption capacity; C is the equilibrium concentration; n , k , K , A , B , W_a and W are the constant parameters for the isotherm equations.

adsorption yield is approximately the same for two samples in low equilibrium concentrations, while the adsorption yield of calcinated dolomite sample is reduced at high equilibrium concentrations. The observed decrease in adsorption yield as a result of calcination can be attributed to the forming of CaO and MgO, which transforms to their hydrolysis products at aqueous medium. Such a transformation can be lead to both changing of the phosphate adsorption mechanism and hindering of the diffusion of phosphate ions to the pores. Also the decrease observed in adsorption yield of the calcinated sample, contrary to no significantly changing of adsorption capacities, makes a sign the removal probability by interacting of the hydrolysis products of the oxides with phosphate ions.

The experimental data fit not to the Langmuir model. This result suggests that phosphate adsorption is not limited with monolayer coverage and the adsorption occurs predominantly through physical interactions. The parameters for the Freundlich isotherms of raw and calcinated dolomite sample under CO₂ atmosphere at 350 °C are given on Table 1. It is seen from this table, that the value of n (a measure of the intensity of adsorption) for raw dolomite sample is higher than that of calcinated dolomite sample. The decrease in the value of n as a result of calcination at 350 °C can be attributed to formation of the pore diffusion resistance regard to adsorption and/or the changing of mechanism of interactions between phosphate ions and dolomite surface. The value of k (a measure of adsorption capacity) for calcinated dolomite sample is higher in comparison with raw dolomite sample. This result suggests that the oxides formed by calcination and the basic medium in micropores produced more suitable conditions for phosphate adsorption.

Table 1 also contains the isotherms parameters and regression coefficients belonging to BET, Halsey, Harkins–Jura, Smith and Henderson adsorption models of raw and calcinated dolomite sample under CO₂ atmosphere at 350 °C, respectively. All these equations are suitable for multilayer adsorption. Especially, the fitting of these equations can be seen in heteroporous solids [24–27]. The large values of the constants for Henderson equation and the high value of y_m obtained from BET equation

indicate the microporous structure is more stable in raw and calcinated dolomite samples. The high y_m value obtained for the calcinated dolomite sample from BET isotherm show that the calcination process leads to microporous structure and large surface area for phosphate adsorption. Also, the fact that calcinated dolomite sample has relatively a higher monolayer adsorption capacity supports the possibility of the change of mechanism. When the k constants for both samples are compared, it can be said that the interactions between phosphate ions and the surface of the calcinated dolomite or the hydrolysis products of the oxides is more effective than that of raw sample.

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