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Research Article

Adsorption of Phosphorous and Zinc, and their interaction and processing power on Bentonite

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Abstract

his work aimed to evaluate isothermic adsorption of Phosphorous and Zinc separately and t
teraction on Bentonite minerals. Five concentrations of each element viz. 0, 50, 100, 150,
)0μgL^{-1}, and their interaction concentrations of 0+0, 50+50, 100+100, 150+150, 200+200μ
ere used. Langmuier equation was used to calculate Xm and k. Estimating quantity and inten
ırves (Q/I) and buffering capacity, as 2.5g of Bentonite was treated with increasing concentrat
: P and Zn using K_2HPO_4 and $ZnSO_4.7H_2O$, respectively, 0, 0.2, 0.4, 0.8, 2 and 4mmol l^{-1}.
ıspension was shaken for 3 hours and left for 24 hours to equilibrate, then the concentration of l
and Zn in the filtrate was extracted and estimated. The relationship between the quantity (adsoı
nount of e element) and the intensity (ionic activity) was drawn. From the slope of the straight
juation, the buffering capacity of the element was calculated. The results showed a signifi
crease in P and Zn adsorbed with the increase in levels of addition. Effect of interaction betw
vo elements showed a significant increase in P adsorbed at the last two levels, whereas no signifi
crease was observed in addition of 50 and 100 μg ml^{-1}. The adsorbed Zn increased as a resu
teraction between two elements. The value of Xm for adsorption of P was 114.94μg g^{-1} in of ad
, and this value was not affected when P and Zn were added together. For Zinc, maximum adsorp
ıpacity value in adding zinc alone was 204.08μg g^{-1}, and the value was similar in adding
ements together. Binding energy (k) was 0.056ml μg $^{-1}$ by adding P alone, and increased slig
hen adding two elements together (0.081μg g^{-1}at adding Zinc), and binding energy was 0.005m
and slightly increased when adding two elements together (0.006ml μg $^{-1}$). The adsorbed amour
. was higher than P and binding energy is lower. Buffering capacity of P in Bentonite was 13.28
kg^{-1} Bentonite, and it is considered an average with its P content whereas, Zinc had 341.84 mg
considering mineral with a high Zinc content.

Keywords: Adsorption, Bentonite, Phosphorous and Zinc, Buffering capacity.

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Introduction

Bolan et al. (1999) pointed out that adsorption is bonding of ions to charged soil surface by electrostatic or specific bonds. It is one of the basic chemical reactions through which ions are trapped on surfaces of soil components. Adriano et al. (2002) and Ali et al. (2014) divided the adsorption process of ions from charged surfaces into specific adsorption and non-specific adsorption. The important soil components in the adsorption process are clay minerals, water mineral oxides, and organic matter. Since the calcareous soils have high carbonates, therefore phosphate fertilizers, when added to soil, are subject to sedimentation and precipitation reactions, as available phosphorous is transformed to available P (Al-Abdali 2005). The study of the adsorption process and how it occurs is important to assess soil contamination with heavy metals, their bioavailability, and their toxicity in plants (Osman 2012).

Bentonite is a silicate mineral of 1:2 type. It consists of two layers of tetrahydra and a layer of octahedra, which are connected by weak van der Walls forces. Therefore, its structural composition is unbalanced, allowing water molecules and cations to enter between layers to balance charges, and mineral has a high exchange capacity and ability to adsorb ions (Mitchell 1999; Nesse 2000). Reyhani et al. (2010) showed a strong correlation between the separation of clay in soil and cations exchange capacity with maximum adsorption capacity of Zinc in calcareous soil. Sheta et al. (2003) showed that Bentonite has a high ability to adsorb Zinc and Iron ions, and its ability to adsorb zinc is more than iron. The most important factors affecting Zinc adsorption are soil reaction, quantity, and type of clay minerals, organic matter content, oxides, and soil type (Peganova & Edler 2004). Properties of Zinc bonding with clay minerals are of replaceable type on clay minerals, while the rest are non-replaceable (Tiller & Hodgson 1962). The main problem of phosphorous adsorption is to find an effective, available, and low-cost material. Bentonite clay is one of the effective materials for phosphorous adsorption, but it requires a long period for phosphorous adsorption (Moharami & Jalali 2013).

Quantity and intensity of elements on clay mineral depending on the relationship between energy level or intensity (I) of the available element and quantity or capacity of the element (Q) present in the solid part of mineral and ready to transfer to the solution, meaning it describes processing strength of the element. This work aims to use the thermodynamic approach to a calculated mathematical description of the adsorption process for phosphorous and Zinc, separately, on Bentonite mineral, the interaction between them, and the effect of one of them on the other in adsorption to calculate maximum adsorption and binding energy of reaction surfaces according to Langmuier equation of one surface and calculating buffering capacity of metal from phosphorous and zinc.

Materials and methods

This experiment was carried out in the Department of Soil Sciences and Water Resources, College of Agricultural Engineering Sciences, University of Baghdad. A sample of Bentonite was used to determine some of its chemical and physical properties, according to Page et al. (1982). To evaluate adsorption of phosphorous and zinc ions, standard solutions of compounds of K_2HPO_4 and $ZnSO_4.7H_2O$ were prepared as sources of phosphorous and zinc, respectively, at five concentrations: 0, 50, 100, 150, 200µg kg^{-1} and for two elements at concentrations of 0+0, 50+50, 100+100, 150+150, and 200+200 for Phosphorous and Zinc in succession to overlap between two elements. For the adsorption experiment, 1g of Bentonite was taken, and 1ml of standard solutions was added. Then its volume increased to 50ml by pure brine $CaCl_2$ (0.01 *N*), left for 24 hours, then shaken for half an hour, and Phosphorous and Zinc were measured in the filtrate. Langmuire's equation was used to calculate Xm and k and find out the effect of one element on the other. The same steps were performed, but with the addition of the prepared concentrations of phosphorous with 1ml of same prepared concentrations of Zinc and reached the volume to 50ml and estimating concentration of both P and Zn in the filtrate.

The linear Langmuier equation was applied to describe the adsorption as follows: (1) the amount of Phosphorous and Zinc adsorbed on the soil surface were calculated for each treatment using equation of X = A-C/ S, where X = of element adsorbed on the surface (µg g^{-1}), A = element added to Bentonite (µg ml^{-1}), C = concentration of dissolved element in solution (µg ml^{-1}) and S = weight of Bentonite, (2) Linear Langmuir equation was used as formula of C/X =1/kXm + C/Xm, where C= concentration (Phosphorous and Zinc) in equilibrium solution (µg ml^{-1}), x= amount (Phosphorous and Zinc) adsorbed on surface (µg g^{-1}), Xm = maximum adsorption capacity (µg g^{-1}) and k = binding energy to Bentonite surface (µg^{-1} ml), and (3) for estimating the quantity and intensity curves (Q/I) and buffering capacity, method proposed by Beckett (1964) was

Table 1. Effect of phosphorus and zinc added on the amount of soluble and adsorbed phosphorous and zinc on surfaces on Bentonite.

	Amount of added phosphorous(μgml^{-1})			
	50	100	150	200
Dissolved phosphorous concentration ($\mu g\ ml^{-1}$)(C)	3.85	12.66	25.28	37.66
concentration of phosphorous adsorbed ($\mu g\ g^{-1}$)(x)	230.75	436.70	326.60	811.70
	Amount of added Zinc (μgml^{-1})			
	50	100	150	200
Dissolved Zinc concentration ($\mu g\ ml^{-1}$)(C)	16.35	35.74	55.31	78.71
concentration of Zinc adsorbed ($\mu g\ g^{-1}$)(x)	168.25	321.30	473.45	606.45
	Amount of Phosphorous and Zinc added (μgml^{-1})			
	50 Zn +50 P	100 Zn+100 P	150 Zn+150 P	200 Zn+ 200 P
Dissolved phosphorous concentration ($\mu g\ ml^{-1}$) (C)	2.19	11.23	19.09	26.95
concentration of phosphorous adsorbed ($\mu g\ g^{-1}$)(x)	239.04	443.81	654.55	865.23
Dissolved Zinc concentration ($\mu g\ ml^{-1}$) (C)	14.11	30.18	49.79	68.92
concentration of Zinc adsorbed ($\mu g\ g^{-1}$) (x)	179.45	349.10	501.05	655.40
$LSD_{0.05}$	Dissolved P	Adsorbed P	Dissolved Zn	Adsorbed Zn
	2.24	9.61	3.34	17.34

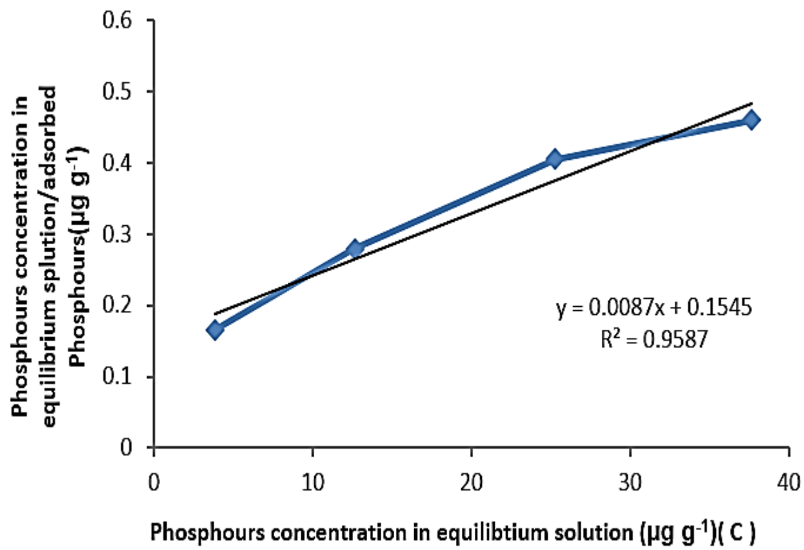

Fig.1. Relationship between concentration of Phosphorous in equilibrium solution on Phosphorous adsorbed and concentration of Phosphorous in equilibrium solution.

used, as 2.5g of Bentonite was treated with increasing concentrations of Phosphorous and Zinc in a manner K_2HPO_4 and $ZnSO4.7H_2O$, respectively, are 0, 0.2, 0.4, 0.8, 2 and 4mmol l^{-1} and fill volume to 25ml with distilled water. The suspension was shaken for 3 hours and left for 24 hours to equilibrate, then extracted and determined the concentration of Phosphorous, Zinc, and other parameters.

Calculating buffering capacity of Phosphorous and Zinc was done as follows: Ionic strength of solutions and ionic activity coefficient was calculated according to Davis (1962) equation, while activity for P and Zn ions was estimated according to Lindsay (1979) using the formula of $-\log fi = AZi^2(\sqrt{I}/\sqrt{1+I}-0.3I)$, where A = constant of 0.509, Zi^2 = square of the charge of the ion, I = ionic strength, which was calculated according to the equation of $I=0.013*EC$. The activity was calculated using the formula of

Table 2. Values of Langmuier equation constants for adsorption of Phosphorous and Zinc on Bentonite.

Treatment	Maximum adsorption capacity ($\mu g\ g^{-1}$) (Xm)	Binding energy ($ml\ \mu g^{-1}$) (k)
Phosphours	114.94	6.43
Zinc	204.08	1.02
Phosphorous (interaction between Phosphorous and Zinc)	114.94	9.31
Zinc (interaction between Phosphorous and Zinc)	204.08	1.22

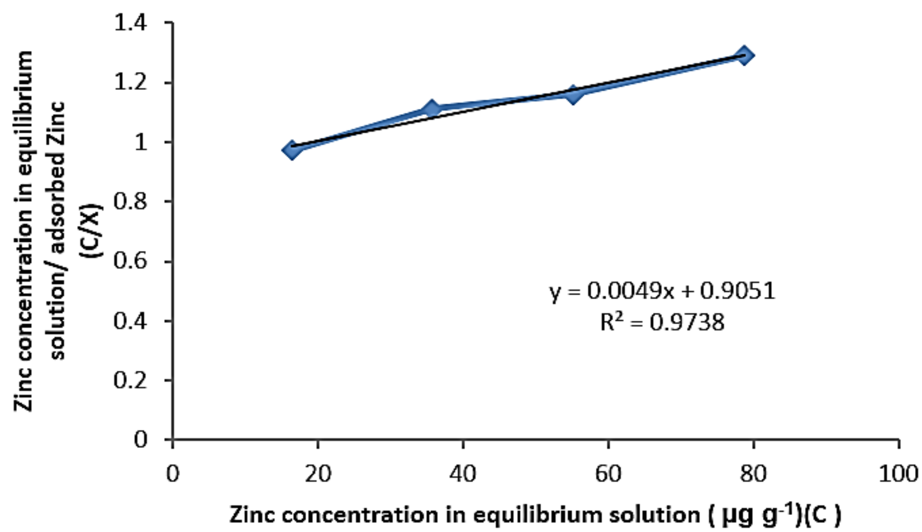

Fig.2. Relationship between concentration of Zinc in equilibrium solution on Zinc adsorbed and concentration of Zinc in equilibrium solution.

I=0.013*EC, a=c*f, where a = ionic activity mol l^{-1} and c = ionic concentration mol l^{-1}. The ion's buffering capacity was calculated from the relationship between quantity (the amount of adsorbed ion) and intensity (ionic activity) and the slope of the straight-line equation.

Results and discussion

Effect of added Phosphorus and Zinc on its soluble and adsorbed quantity: Table 1 shows the effect of phosphorous addition on soluble and adsorbed Phosphorous on the surfaces of Bentonite. A significant increase in the dissolved phosphorous was observed with the Phosphorous addition i.e. adding 3.85 to 12.66, 25.28, and 37.66µg ml^{-1} P addition were led to 50, 100, 150, and 200µg ml^{-1}, respectively, increase in dissolved phosphorous to Bentonite. There was a significant increase in the adsorbed Phosphorus with an increase in Phosphorous addition, as values rose from 230.75 to 436.70, 623.60, and 811.70 µg g^{-1} for additional levels of 50, 100, 150, and 200 µg ml^{-1}, respectively (Table 1).

Table 1 also shows the effect of added Zinc on dissolved and adsorbed Zinc on surfaces of Bentonite. A significant increase in dissolved Zinc was observed with added Zinc of 16.35 to 35.74, 55.31, and 78.71µg ml^{-1} to the levels of 50, 100, 150, and 200µg Zn g^{-1} to Bentonite, respectively. The adsorbed Zinc increased from 168.25 to 321.30, 473.43 and 606.45µg Zn g^{-1} to levels of Bentonite Addition of 50, 100, 150, and 200µg ml^{-1}, respectively. An increase in the adsorbed phosphorous with the increase in levels of addition may be due to the cations exchange capacity of Bentonite, as there are many sites that can adsorb the Phosphorus. These results are consistent with findings of Ofocfule & Okonta (1999), who showed that there are wide applications for clay minerals,

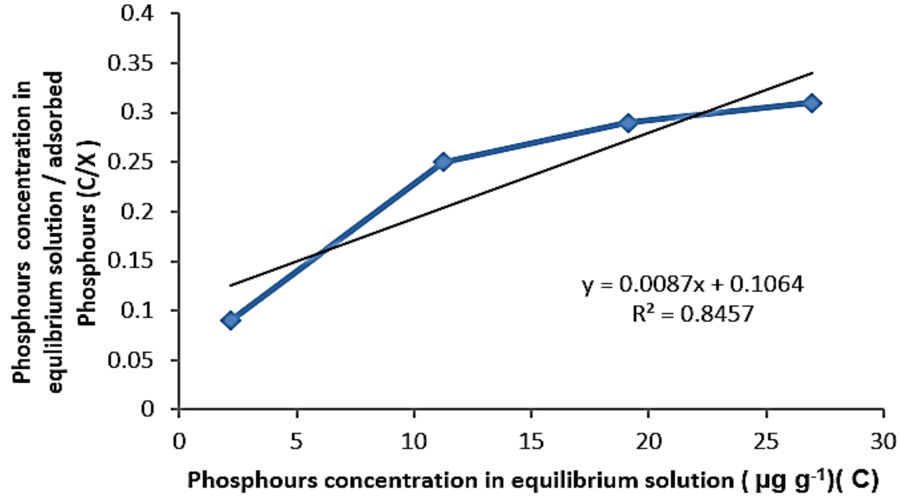

Fig.3. Relationship between concentration of Phosphorous in equilibrium solution on Phosphorus adsorbed and concentration of Phosphorus in equilibrium solution for interaction between Phosphorous and Zinc.

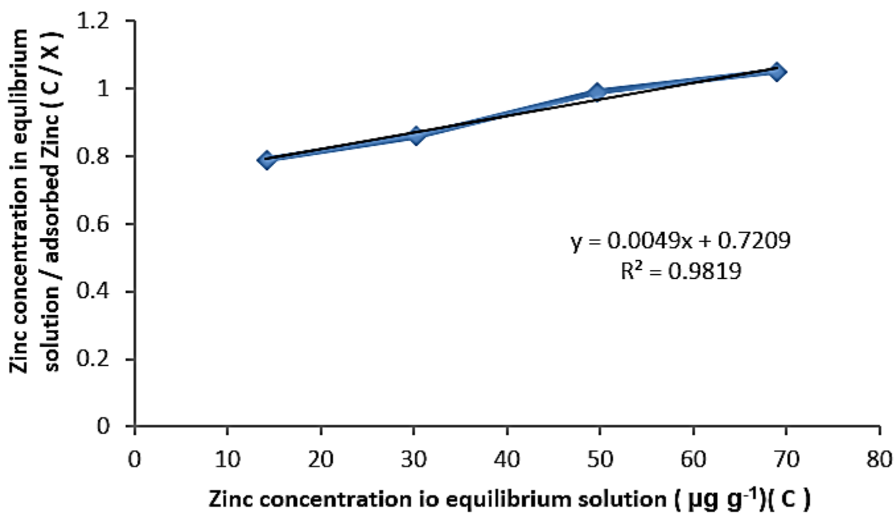

Fig.4. Relationship between concentration of Zinc in equilibrium solution on Zinc adsorbed and concentration of Zinc in equilibrium solution for interaction between Phosphorous and Zinc.

including Bentonite, in fields of pollution treatment because of its high ability to remove, sequester or adsorb large quantities of elements as a result of its high surface area and large porosity. It is used in column chromatography as an adsorbent for many elements and compounds. An increase in Zinc adsorption with increasing levels of its addition is consistent with the results of Reyhani et al. (2010) that indicated a significant correlation between clay content and maximum adsorption capacity.

Interaction between Phosphorous and Zinc: The effect of interaction between Phosphorous and Zinc on the soluble and adsorbed elements in Bentonite showed a decrease from 25.28 and 37.66 to 19.09 and 26.95μg P g^{-1}, respectively, while the decline was not significant at the first two levels (50 and 100μg ml^{-1}) (Table 1). These results are consistent with the findings of Al-Ashour (2010), which showed that adding high levels of P and Zn leads to a lack of readiness due to interaction between them and their precipitation as Zinc phosphate. On the other hand, the interaction between P and Zn significantly increased the Phosphorous adsorbed at the last two levels, i.e. the values increased from 623.60 and 811.70 to 654.55 and 856.23μg P g^{-1} Bentonite, respectively. There was no significant increase in the addition levels of 50 and 100μg ml^{-1}. As for Zinc, there is a significant decrease in its soluble level as a

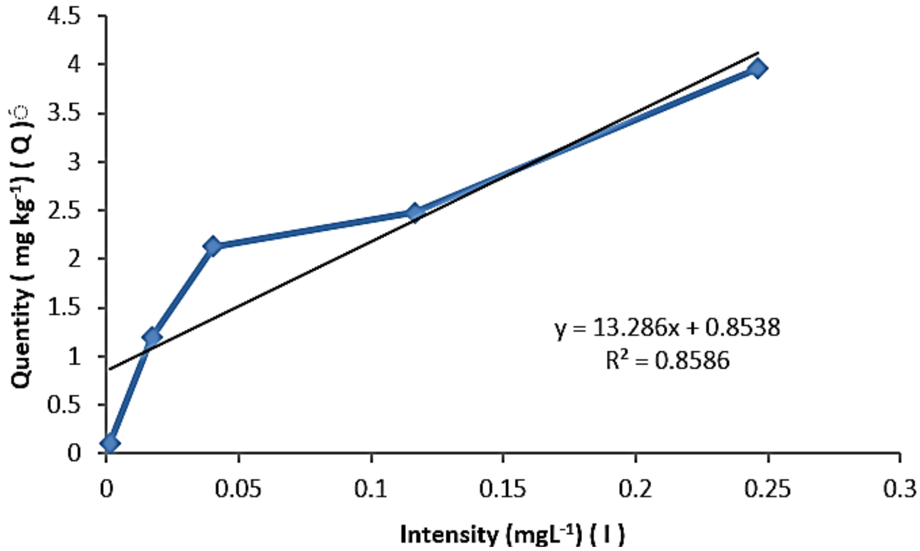

Fig.5. Relationship between quantity and intensity of Phosphorous in Bentonite.

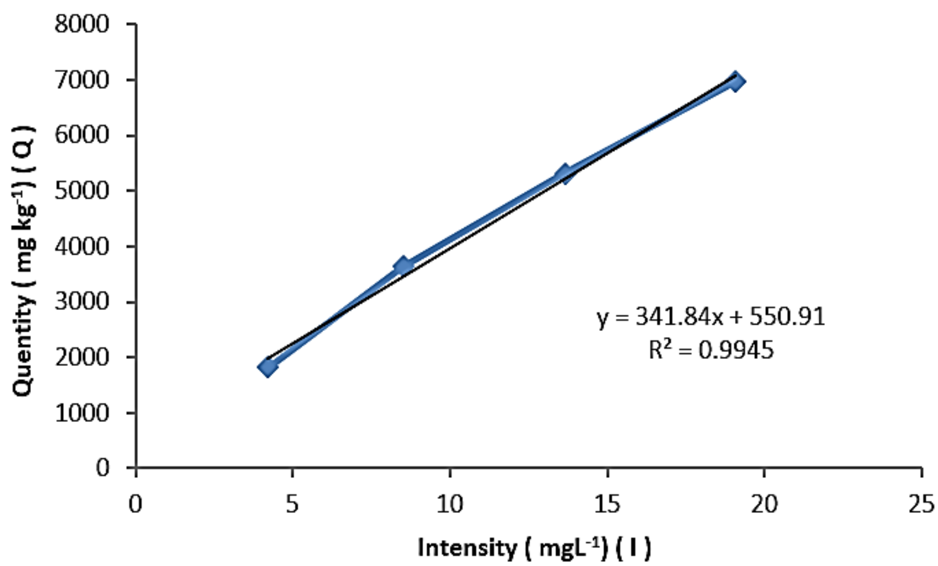

Fig.6. Relationship between quantity and intensity of Zinc in Bentonite.

result of interaction between two elements at levels 100, 150, and 200µg Zn ml^{-1}, and the values decreased from 74.0, 55.31, and 78.71µg Zn ml^{-1} Bentonite to 30.18, 49.79 and 68.92 µg Zn ml^{-1} Bentonite, respectively. These decreases were not significant at the level of 50µg Zn ml^{-1}. These results are consistent with findings of Farah & Soliman (1987) and Qabaa (2000) that showed the presence of Phosphorous in the solution leads to a decrease in the availability of Zinc due to the negative interaction between them and their precipitation as Zinc phosphate, especially at high levels of it. On the other hand, the adsorbed Zn increased due to interaction between them for levels 100, 150 and 200µg Zn g^{-1}, as 321.30 and 473.45 and 606.45 to 349.10, 501.05 and 655.40µg Zn g^{-1} Bentonite, respectively, and these decreases were not significant at first level. An increase in adsorbed P and Zn as a result of interaction between them may be due to an increase in the concentration of ions, which leads to a rise in the pressure of the electric double layer, which leads to an increase in the proximity of ions to surfaces of Bentonite, which leads to an increase in adsorbed amount.

Use Langmuier equation to describe adsorption process: Langmuier equation was used to describe the adsorption of P and Zn on Bentonite (Figs. 1-4). Table 2 shows values of adsorption equation constants, which are maximum adsorption capacity (Xm) and binding energy (k). Values of Xm give an idea of the adsorbed element that for adsorption of P was 114.94μg g^{-1} when adding P alone, and value not affected when P and Zn were added together. This indicates that there is no competition between two ions on exchange surfaces of Bentonite similar to Zn. The maximum adsorption capacity was reached at the addition of Zn alone 204.08μg g^{-1}, and the value remained the same when adding two elements together. These results show that the maximum adsorption capacity of Zn is higher than P. This may be due to the adsorption mechanism on surfaces of Bentonite. Phosphorous is not free form in solution, as it binds with oxygen and hydrogen in the form of lagind and $HPO_4^{=}$ or $H_2PO_4^{-}$ according to pH value, which is an anion in this form and its bonding with Bentonite, by other positive ions that adsorb to surfaces of mineral and act as a bridge to link P ions with it. It is an indirect method of adsorption or replacing hydroxyl ions OH-, which also depends on pH value. Therefore, the adsorbed amount is less than the positively charged Zn ion, which is directly adsorbed on metal surfaces due to the difference in charge. Thus it is faster in the adsorption process and the amount of adsorbed is higher.

Binding energy (k) was 0.056ml μg $^{-1}$ at adding P alone. This indicates P adsorption process is done indirectly by building a bridge between Phosphorous and cations adsorbed on surfaces of the metal, which has two or more positive charges. The value of k slightly increased when adding P and Zn together, reaching 0.081ml μg-1 at Zinc, and binding energy was 0.005ml μg-1 and slightly increased at adding P and Zn together 0.006ml μg^{-1}, thus adsorbed Zn is higher than P and at low bonding energy.

Buffering capacity of Phosphorous and Zinc: Figure 5 displays buffering capacity of P in Bentonite, which was obtained from the slope of the straight line of quantity and intensity relationship (Q/I), expressed as mg kg^{-1}, which was 13.28mg P kg^{-1} Bentonite. It is considered medium with its P content, indicating that the mineral possesses an average buffering capacity of P i.e. ability to be processed with P is medium. This is due to the nature of Bentonite, which has a low-medium content of P. Buffering capacity of Zn on Bentonite mineral was 341.84mg kg^{-1}, thus, the mineral is considered to be high in Zn content (Fig. 6). The mineral possesses a high buffering ability against changes taking place in relation to Zn levels in Bentonite solution through equilibrium with other forms of Zinc and a high ability of the metal to supply Zn. These results agree with the findings of Saleem (2005) that showed the buffering capacity of Zn increases with the increase of Zn added to the soil.

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