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The effect of plant and animal wastes and zeolites on boron adsorption in different soils textures

Riyadh S. Bedeeh[1], Mohammed A. Abdulkareem[2] and Salwa J. Fakir[2]
[1]Soil Science and Water Resources Dept., College of Agriculture, University of Sumer, Iraq
[2]Soil Science and Water Resources Dept., College of Agriculture, University of Basrah, Iraq

Abstract

The experiment was conducted in the laboratories of the College of Agriculture, University of Basrah at different Soils of Basrah Province, southern Iraq, to study the effect of organic materials and zeolites on boron adsorption. zeolite was added at levels of (0, 20, 40) $ton.ha^{-1}$, cow manure and plant residues was added at levels of (0, 25, 50) $ton.ha^{-1}$and biochar was added at levels of (0, 15, 30) $ton.ha^{-1}$. soil was wetted at field capacity moisture and incubated at 30°C for a period of 15 days. Boron was added to the soil at levels of 10, 20, 40 $\mu g.g^{-1}$ soil in the presence of $CaCl_2.2H_2O$ 0.1*M* salt and the soil was agitated for three periods (1, 24, 48) hs. The equilibrium concepts tested the Isothermal of adsorption equations (Langmuir, Freundlich). The results showed that the Freundlich equation was more efficient in describing the boron adsorption according to the values of the determination coefficient (R^2), which gave the highest value of 0.999. While, zeolite and biochar were excelled in adsorption of boron compared to other materials. The amount of adsorbed boron increased with increasing the levels of boron and added materials for soil.

Key words: organic residues, Isothermal models, Boron adsorption, zeolites

Introduction

Boron is one of the essential nutrients for plants and it is ranked as the seventh of the microelements needed for plant growth (Gupta, 1993). It is considered as one of the micro-nutrients and has an important role in plant life. However, increasing its concentration in plant tissue is considered phytotoxic (Feigin *et al*., 1991).The range between the ideal level of plant needs and the harmful and toxic quantity of it is very small, and these two levels differ according to the different plants. This case gives importance to study boron, especially in areas where agricultural lands are exposed to boron processing continuously. The plant absorbs boron from the soil solution in the form of H_2BO^{-3}, HBO_3^{-2}, $BO_3^{-3}$and $B_4O_7^{-2}$.The availability of these boron forms depends on the chemical and physical properties of soil, such as carbonate minerals , organic matter, soil pH, soil salinity, clay and wetting and drying cycles (Abidnias *et al*., 2007 and Hoshan, 2016).

The mechanism of adsorption of ions in the soil controls the availability of plant nutrients, and this process is greatly influenced by the properties of the soil (Prasad *et al*., 1997). This mechanism is important to understand the behavior of boron in the soil and its availability to plant. The amount of boron absorbed by the soil increases with the increase of added Boron, depending on the type of adsorbed fraction and the temperature (Kumari *et al*., 2017 and Tamuli *et al*., 2017). Using thermally isothermic adsorption curves can reflect the amount of material adsorbed by the adsorbent at during equilibrium stste and a constant temperature (Gupta, 1993).

Organic materials are considered as an economical and cheap materials in nature, where the results of many studies have confirmed that increasing the soil content of organic matter from 0.5% to more than 0.75% increased the adsorbed boron in the soil by 47.6 - 60% and that there is a positive correlation between soil organic matter content and boron fixation (Goldberg and Forster, 1991). Gupta (1984) reported that the addition of organic matter increased the adsorption of boron at the exchange surfaces, and Ferracciu *et al* (2000) confirmed the ability of organic matter to increase boron adsorption. Hoshan (2016) obtained boron adsorption of 10.18 mg kg^{-1} when soil treated with 4% cow manure.

Adding zeolite to agricultural soils contaminated with heavy elements reduced the absorption of heavy metals by plants and reduced their toxic effect on plants. Kumar *et al*. (2007) demonstrated the ability of the natural or industrial zeolite to adsorb boron and reduce its harmfull. The use of 20% of the zeolite with 80% contaminated soil reduce contamination with many elements, including boron. In addition to zeolite, biochar was used to protect the environment from contaminated as a porosity substance that can be added to the soil to improve its properties and reduce environmental contamination (Peake, 2015). This study conducted due to the lack of studies related to the use of natural materials in boron adsorption within southern Iraqi soils. Such materials available naturally as a cheap constituent .The aim of this study is to understanding of the mechanism of boron ion adsorption by these materials and the reduction of its harmful effect on plants when irrigation with water with a high content of boron, especially in arid and semi-arid regions including Iraq (Yau *et al*., 1995). As well as, studying mathematical models that describe the adsorption mechanism under different conditions of the quantity and quality of adsorption material.

Materials and methods

Soil samples (0 – 30 cm) were collected from two agricultural lands in Basrah Provico (Al-Zubair and Al-Madina) with different properties. The samples were air - dried and passed through a (2) mm sieve. Some of the chemical and physical properties of soils were estimated according to the standard methods of analysis mentioned in Page *et al* (1982), Black (1965) and Jackson (1958) as shown in Table (1).

Table (1) Some chemical and physical properties of the study soils

Soils	pH (1-1)	EC (1-1)	CEC	O.M	CaCO3	Clay	Silt	Sand	Avaliable B
		ds.m-1	Cmol +Kg-1	gKg-1					µgg-1
Al-Zubair	8.17	4.60	4.96	3.42	293.20	90.33	50.50	850.15	2.82
Al-Madina	8.07	6.14	13.95	14.85	350.50	490.90	420.60	170.40	3.39

Two types of organic materials were used chosen, which are cow manure (M) and plant residues (P) (wheat: Alfalfa at a ratio of 1: 1). after composted for 70 days with water at a ratio of 1:2. In addition to organic materials, zeolite (Z) and biochar (B) were used in the study and some of its initial properties were estimated according to the methods mentioned in Page *et al* (1982). 1 kg of air- dried soil was taken, grined and Passed from a sieve of (2 mm) . Zeolite was added three levels (0, 20, 40) tons.ha^{-1} while cow and plant residues were added at levels 0 , 25 and 50 tons.ha^{-1} and Biochar was added three levels 0, 15, 30 tons.ha^{-1}. Soil samples were moistened with water to the limits of the field capacity of each soil and incubated at 30 °C for 15 days and maintaining a constant level of water in the soil within the field capacity during the incubation period.

Boron adsorption experiment was conducted by taking 10 g of each soil sample after the end of the incubation period and placed in 100 ml plastic tubes boron was added at 5, 10and 20 cm^3 of a standard solution (100 mg B L $^{-1}$) in the form of boric acid H_3BO_3. Each tube was treated with 5 ml of a solution (0.1 *M* $CaCl_2.2H_2O$) then complete the volume with distilled water to 50 ml to obtain 10, 20 and 40 mg.B L^{-1} . These groups were replicated three times for each soil, then the tubes were closed and shaken for periods of 1, 24 and 48 hours with a mechanical shaker at a temperature of 25°C. The number of experimental units of the study soil would be 648 (2 × 3 × 12 × 3 × 3) for is. (Soil × Boron levels × treatments × periods × replicates) . After the end of each shaking period, soil reaction pH of the suspension is measured by a pH-meter device. The equilibrium solution was separated from the soil by filtering through filter paper and the electrical conductivity boron concentration by Curumin method were estimated . The amount of boron adsorbed of the soil surface was calculated (µg. g B $^{-1}$ soil) from the following equation:
$q = (C_o – C) \times V/W$
q : the amount of boron adsorbed on the surface (µg.g^{-1}), Co : the initial boron concentration (µg ml^{-1}), C : the boron concentration in the equilibrium solution (µg.ml^{-1}), V : the volume of the total extraction solution (ml) and W : weight of soil (g)
Applying the Langmuir isotherm model of thermal isotropic adsorption to the data for the boron after taking linear equation: Type (II) $Ce / qe = (1 / qmK_L) + (Ce / qm)$
whereas :
qe : amount of boron ion adsorbed at the surface (µg.g^{-1}), Ce : boron concentration in equilibrium solution (µg ml^{-1}), K_L : binding energy (ml µg^{-1}) and qm : adsorption capacity (µg.g^{-1}).
The adsorption data was also applied to the Freundlich isotherm equation after taking the linear equation: $\text{Ln } qe = \ln K_f + n^{-1} \ln Ce$.
Where: n^{-1} and K_f are Freundlich model constants, qe : the amount of adsorbed boron per unit weight (mg Kg^{-1}) and Ce : the concentration of boron in the equilibrium solution (mgL^{-1}).

Results and Discussion

Factors affecting Boron adsorption

Primary concentration

The results obtained in Figs (1, 2, 3) indicated there was a significant increase in the amount of boron adsorbed with an increase in the levels of boron , organic materials and the reaction period of the of the two study soils. The Al-Madina soil recorded the highest amount of adsorbent (37.36) $\mu g.g^{-1}$, followed by the soil of Al-Zubair (23.57) $\mu g.g^{-1}$ along with the addition of 40 μg. cm^{-3} B (Figure 1). Mohammed and Sufyan ,2011, Kumari *et al*, 2017) concluded: that increasing the boron concentration in the soil solution increased boron absorbed by the soil.

Reaction time

The results showed that the reaction time of 48 hours gave the highest amount of B Al-Medina soil which reached (23.08) $\mu gB.g^{-1}$soil compared to Al-Zubair soil which reached (15.50) $\mu gB.g^{-1}$ soil (Fig.2) This may be due to the rapid saturation of specialized and non-specialized sites of boron adsorption, which may occur in the first hours of the equilibrium period, where a high percentage of the added boron is associated with soil components, followed by slow diffusion of boron within the crystal structure of the clay minerals. The results agrees with Alwan (1989).

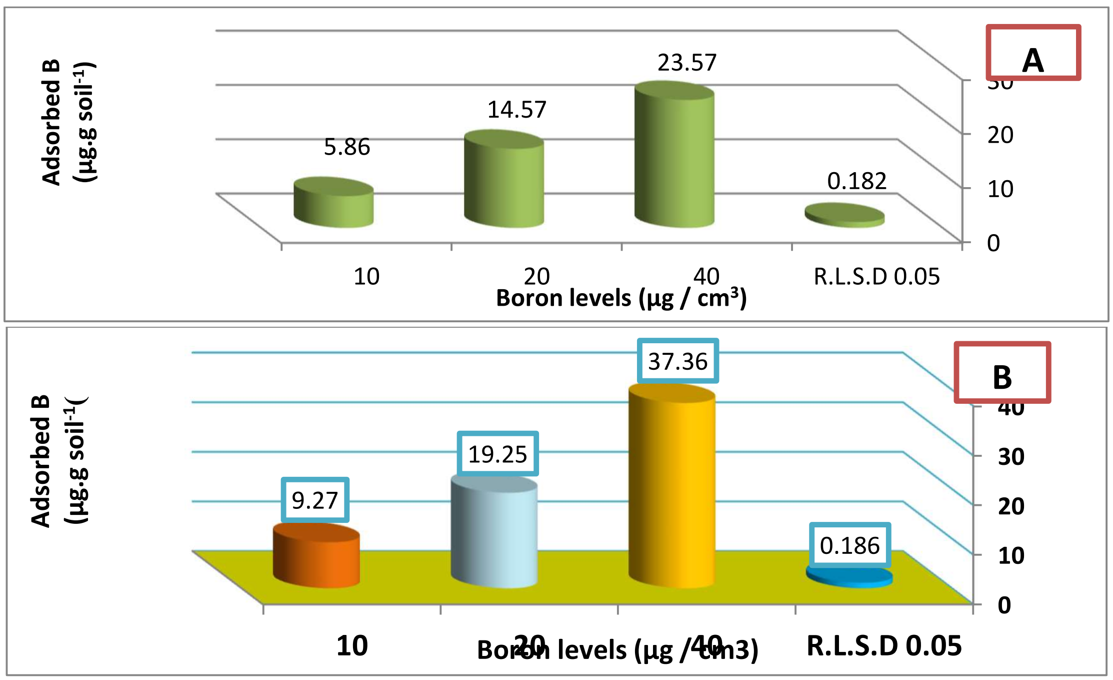
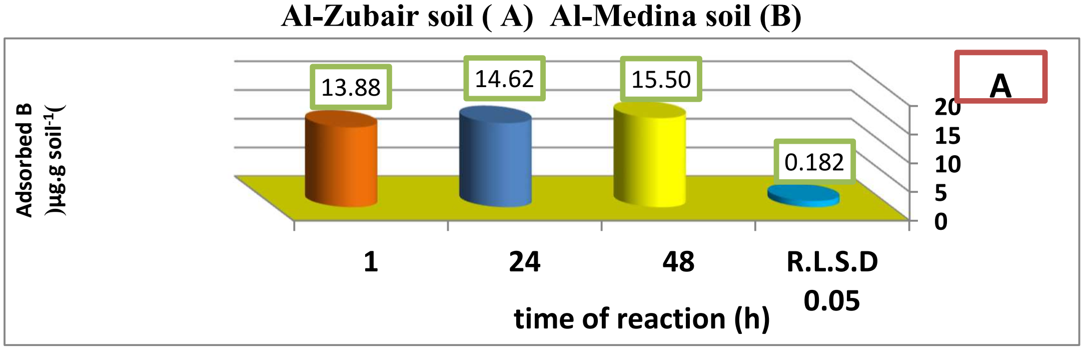


Figure (1) The effect of boron levels on the adsorbed amount of boron in the study soils Al-Zubair soil (A) Al-Medina soil (B)



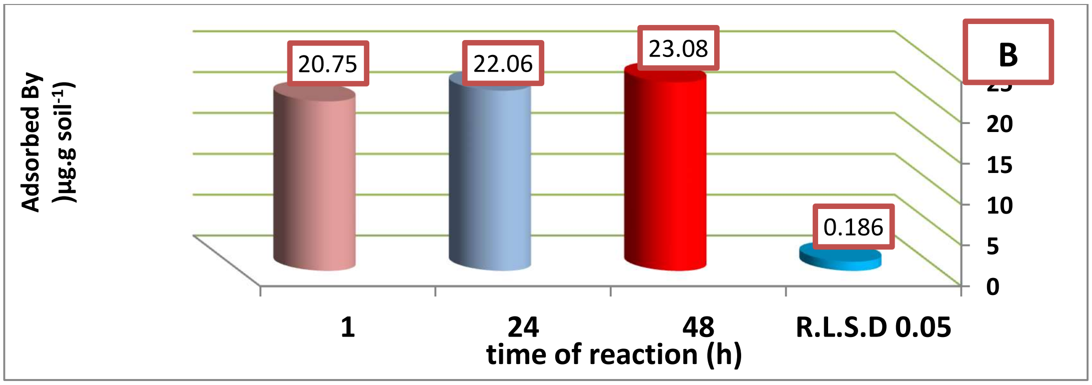


Figure (2) The effect of the reaction time on the adsorbed amount of Boron in the study soils Al-Zubair soil (A) Al-Medina soil (B)

The level of added materials

The amount of boron adsorbed increased with increasing the levels of added materials (zeolite, Biochar, cow manure and plant residues) compared to the first level and the control treatment (Fig. 3). The level of 40 $kg.ha^{-1}$ zeolite added to the Al-Medina soil resulted the highest adsorbent amount of boron was (26.52 $\mu gB\ g^{-1}$) followed by Al- Zubair soil (19.59) $\mu g.B\ g^{-1}$ soil and this is due to the porous composition of zeolites . zeolite improved the physical, chemical and biological properties of the soil (Ghazavi, 2015 and Di Giuseppe *et al*, 2015) and thus increased the amount of boron adsorbed in soil. The materials can be arranged according to their efficiency in boron adsorption by soil as follows:

Zeolites> Biochar > Cow manure> Plant Residues

The amount of boron absorbed by the soil varied with different soil properties and boron levels. Al-Madina soils, with a fine texture and high content of calcium carbonate and organic matter, excelled on their high boron adsorption compared with Al-Zobair soils of coarse texture and low content of organic matter. The results of our study were identical with what was found by Communar and Keren (2006) which obtained significant correlation between the amount of adsorbed Boron and the increase in soil content of clay. (Al-Obaidi and Kashmolahh(2007) and Arora and Chahal(2010) also obtained an increase in boron adsorption with high clay soil content.

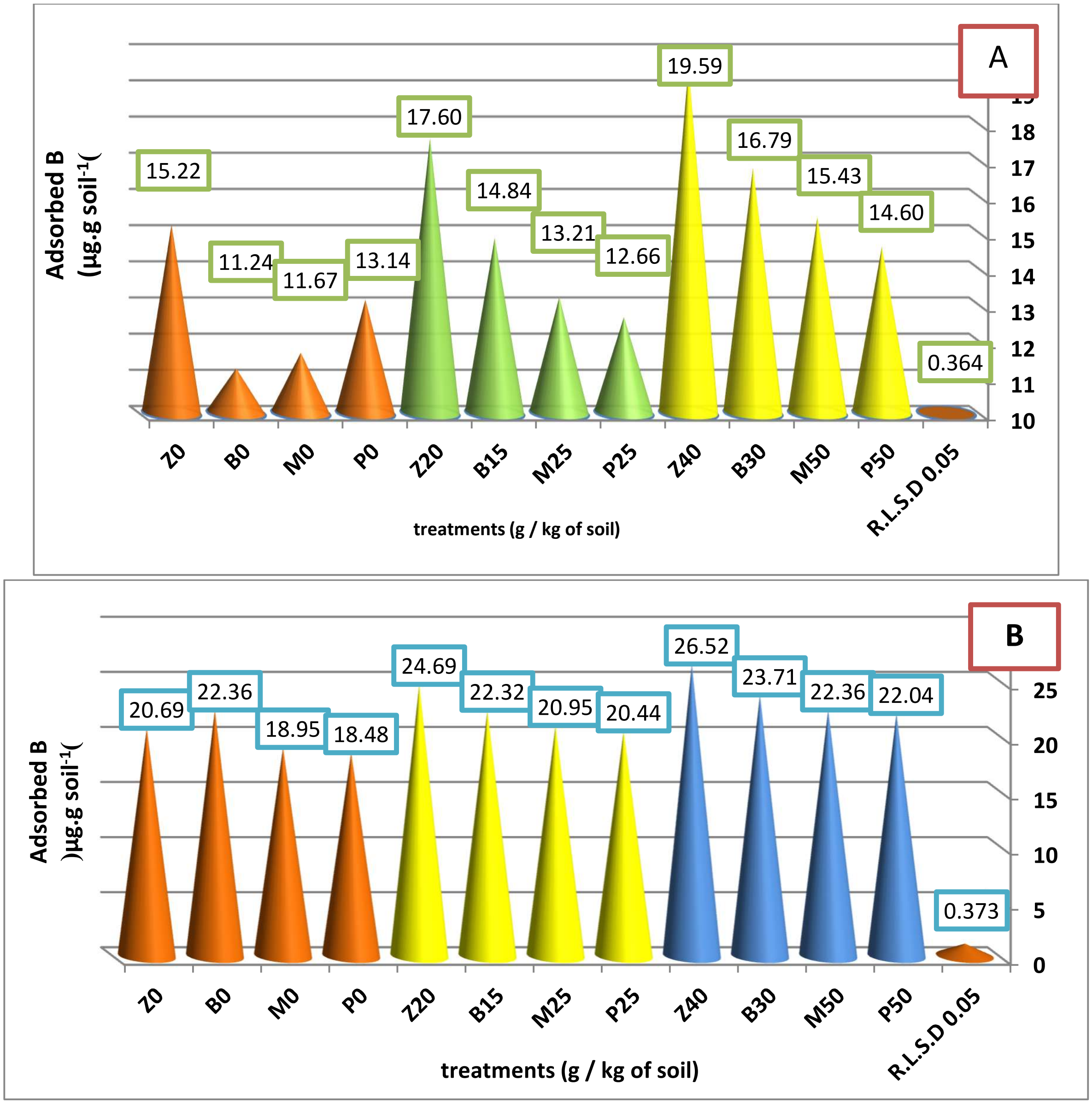


Figure (3) The effect of quantity and quality of added materials on the amount of boron absorbed in the study soils (Al-Zubair soil (A) Al-Medina soil (B)

Use of adsorption Models to characterize boron adsorption:-

To describe the behavior of boron the Langmuir and Freundlich equations were used in a range of boron concentrations (0 - 40) $\mu g.cm^{-3}$ and at 24 hour reaction time. The values of determination coefficient (R^2) are adopted as a standard for comparison between the parameters. The results of Table (2) and Figures (4, 5, 6 and 7) showed that the adsorption equations succeeded in describing boron adsorption in the studied soils, but these equations differed according to the different studied soils and added materials and this is due to the multiple and different adsorption sites on the surfaces of soils and added materials . The results of Table (2) showed the superiority of the Freundlich equation in the linear form in giving of $0.991 \leq R^2$ compared to other treatments used for (zeolite, biochar, cow manure and plant residues). This is consistent with what was obtained by (Datta Bhadoria(1999) and Al-Falahi(2000) who confirmed the success of the Freundlich equation in describing boron adsorption.

Table (2) the determination coefficient of (R^2) for the equations used describe the boron adsorption in the studied soils

Soils	Treatments	The Langmuir equation	The Freundlich Equation
Al-Zubair	Zeolites	0.988	0.995
	Biochar	0.988	0.994
	Cows' manure	0.961	0.991
	Plant residues	0.942	0.992
Al-Madina	Zeolites	0.955	0.993
	Biochar	0.922	0.999
	Cows' manure	0.918	0.999
	Plant residues	0.909	0.999

The results of Al-Amiri *et al*.(2014) indicated that the Freundlich equation was the most efficient of the Langmuir equation in describing the adsorption of boron and zinc in calcareous soils based on the value of the determination coefficient (R^2), which amounted to 0.931 and 0.887, respectively. The results shown in Figures (5 and 7) that the Freundlich equation can give a good description of the reaction within the boron concentrations used in the study (0 - 40) µg. cm^{-3} for all studied soils and added materials the adsorption points were more consistent with the straight line, and to reach a single straight line means a single layer of boron adsorption reaction on soil colloids. This shows the possibility of applying the Freundlich equation to better describe the boron adsorption for samples of soils and the added materials compared to the simplified Langmuir equation (which proved its validity to describe adsorption in some soils (Fig. 4and 6) The results of our study were identical with results of the Kashmolah(2003) and Al-Amiri *et al*.(2014). The findings of Dey *et al*.(2013). through the study of 12 agricultural soils in India medicated that, the Freundlich equation was the most efficient among the equations used to describe boron adsorption from soil by giving it the highest value of the determination coefficient (R^2). As we can see from Figure (6) for Al-Madina soil, there are anomalies of the adsorption points from the linear formula of Langmuir equation which explained by Griffin and Burau (1974). to the multiple of the boron adsorption mechanism.

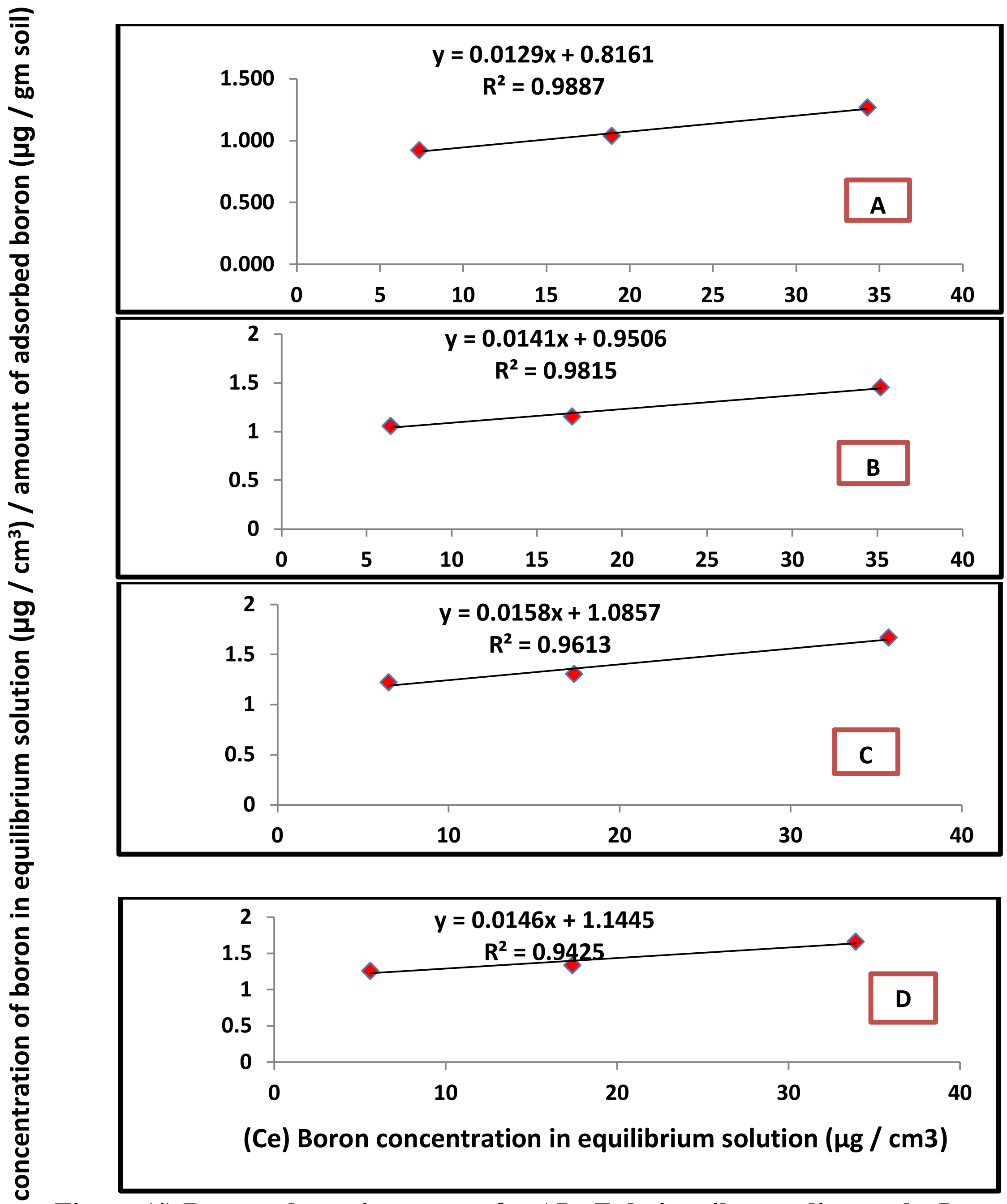


Figure (4) Boron adsorption curves for AL- Zubair soil according to the Langmuir equation for Zeolites (A) Biochar (B) Cow manure (C) and Plant residues (D)

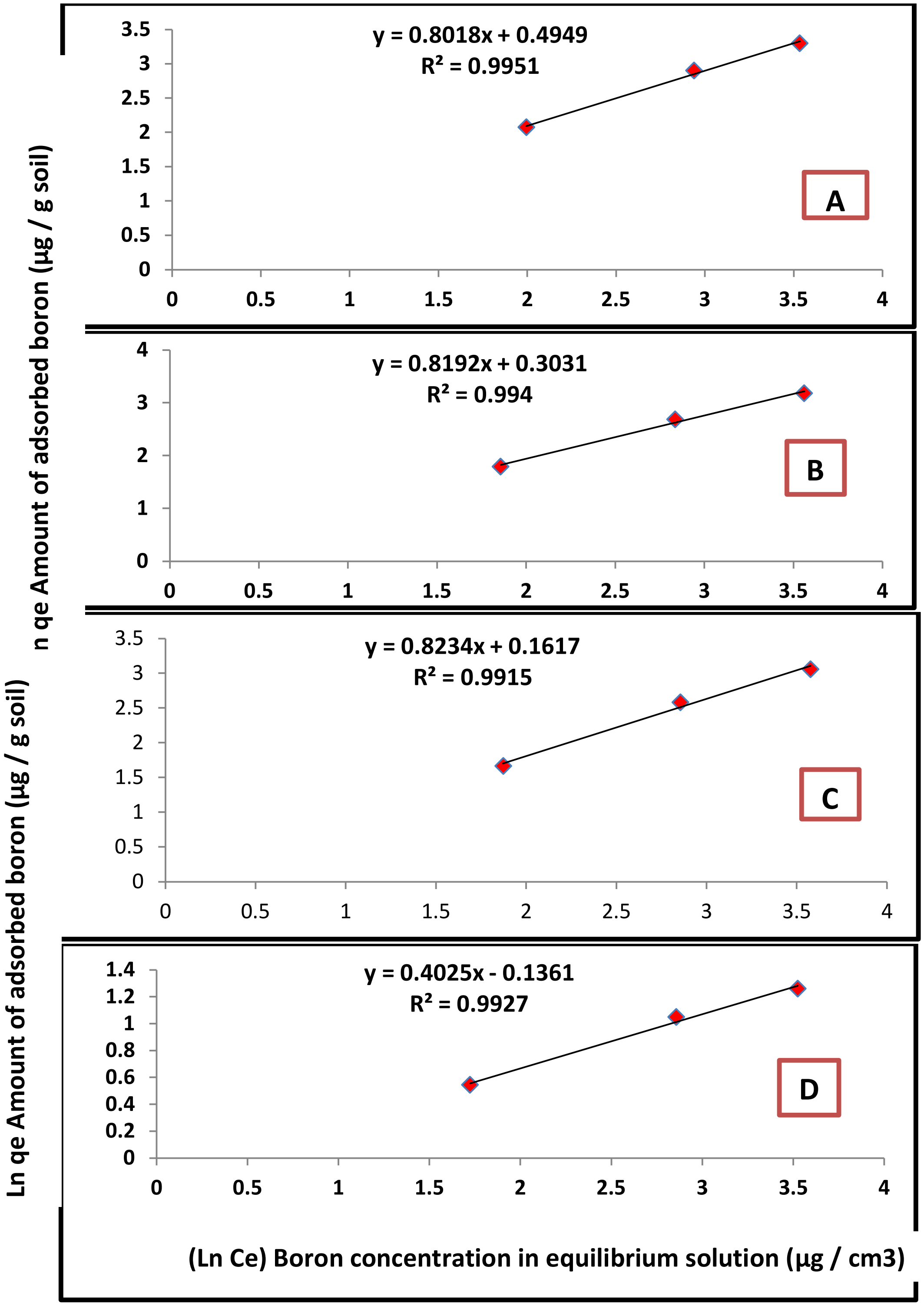
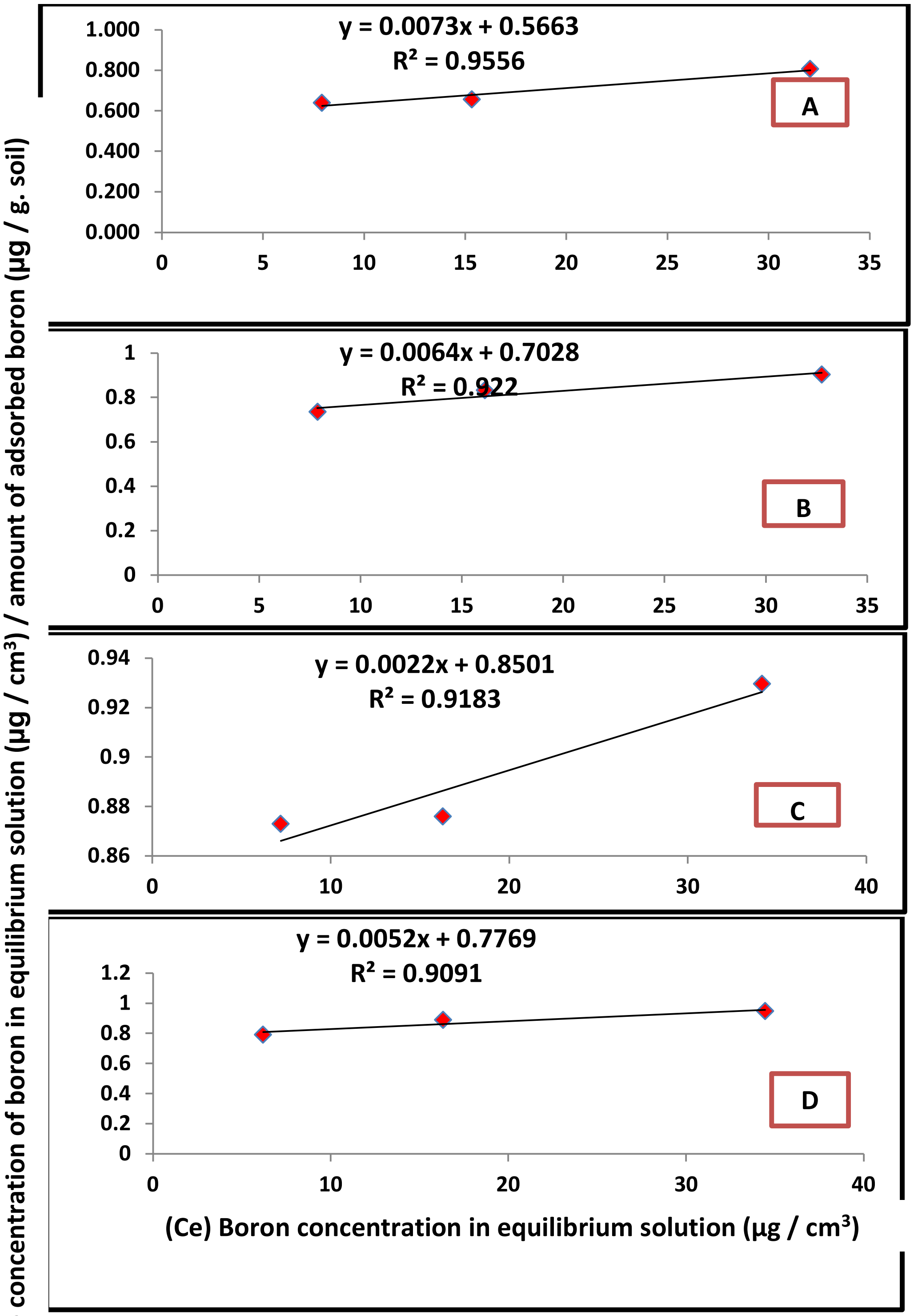


Figure (5) Boron adsorption curves for AL- Zubair soil according to Freundlich equation for Zeolites (A) Biochar (B) Cow manure (C) and Plant residues (D)



Fi 6) Boron adsorption curves for Al-Medina soil according to the Langmuir for Zeolites (A) Biochar (B) Cow manure (C) and Plant residues (D)

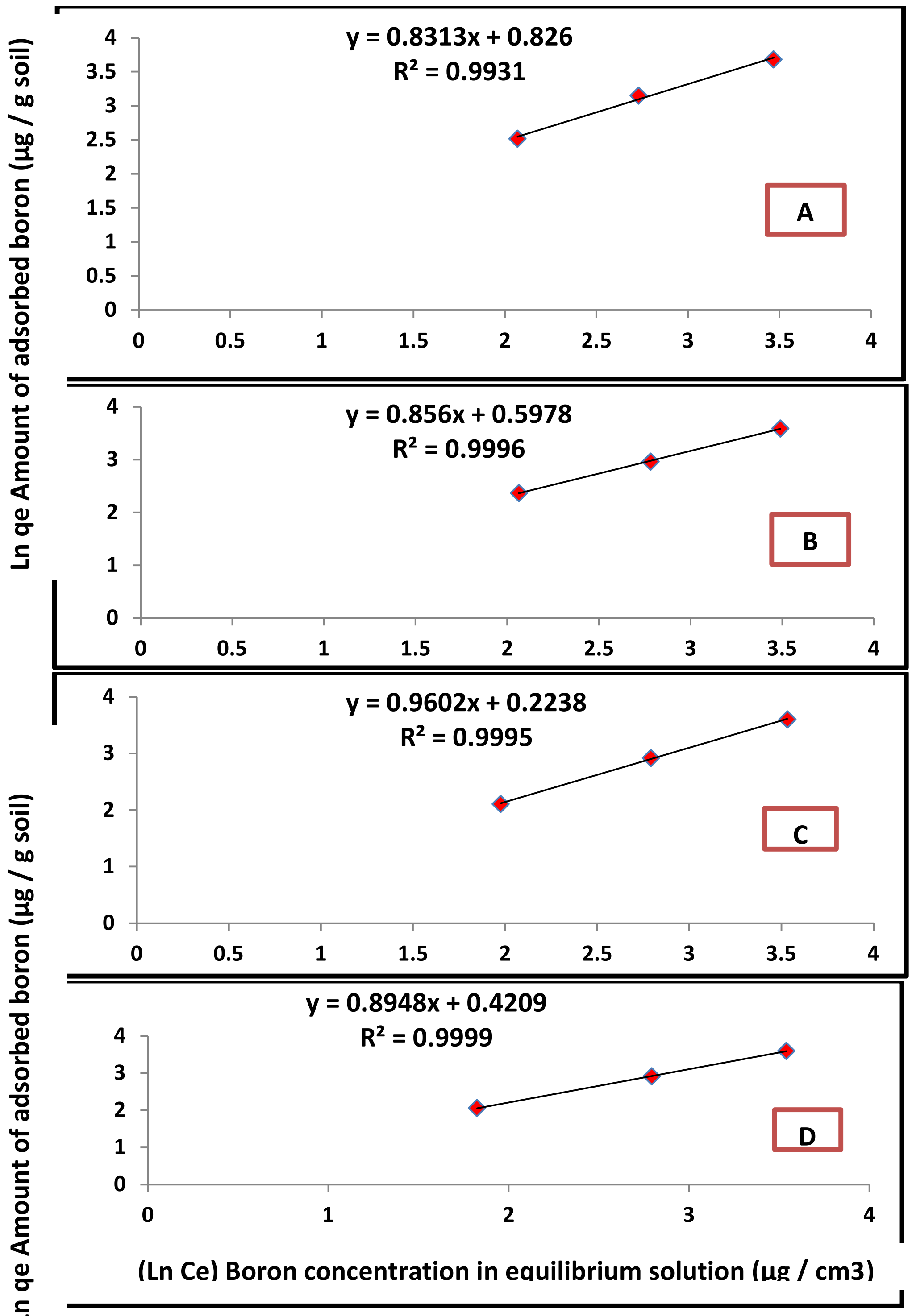


Figure (.) Boron adsorption curves for Al-Medina soil according to Freundlich equation for Zeolites (A) Biochar (B) Cow manure (C) and Plant residues (D)

Use of adsorption equation constants to describe boron adsorption

The statistical significance of the simple correlation coefficient (r) was tested between the amount of boron adsorbed and the concentration of boron in the equilibrium solution. The results in Table

(3) showed that the values of the correlation coefficient (r) were significant for all equations and for all the studied soils and added materials. Where the values of r 0.9534 for fine texture soil (AL-Medina) and their added materials (zeolite, Biochar, Cow Manure, and plant residues), While the values of (r) increased in coarse soil (Al-Zobair) to r ≥ 0.9708 at using the Langmuir equation. As for the Freundlich equation, higher values of (r) were recorded in the study soils compared to the Langmuir equation, where the values of r≥ 0.9965 for fine soil and r ≥ 0.9957 for coarse soils. According to the results of the study (Table 3), the Freundlich equation was more efficient in describing the boron adsorption by soils and added materials compared to the other equations which showed higher values for the simple correlation coefficient, but less compared to the Freundlich equation. The results of our study were identical with what was found by Shafiq(2008) and Al-Ameri(2013).

The zeolite and biochar were resulted the highest values of the correlation coefficient(r) compared to other added materials for all the equations used and both soils study.

In order to compare the efficiency equations in describe boron adsorption in the study soils, the constants of the adsorption equations were calculated (Table 3). These constants were used to describe the adsorption properties of the soil such as the standard of the maximum adsorption (qm) and the standard for the boron binding energy (k) on adsorption surfaces. The results indicated that there is a large differences between the studied soils samples and the materials and equations used in terms of the constants of these equations (qm, k). The values of binding energy coefficients (k) were less and the values of the maximum adsorption (qm) were higher in fine soil **(**AL-Medina) compared to coarse soil (Al-Zobair soil). The low binding strength means the easy release of Boron in soils and vice versa compared to the high binding forces. These results were consistent with the results of Alwan(1989) and Al-Falahi (2000). The results of O'connor *et al*. (1983) , Alwan(1989) , Kashmolah(2003) and , Al-Ameri (2013).indicated that soil contain a limited number of adsorption sites have high activity and greater binding energy compared to other soils that contain a large number of adsorption sites, and this explains the high values of the binding energy coefficient ((k) and the lower values of (qm) in Al-Zubair soil compared to the soft soil of Al-Madina soil. which has a large number of adsorption sites due to its high content of clay and calcium carbonate. Calcium carbonate acts as a collector (Sinkhole) for boron in calcareous soils, thus increasing its holding in the soil (Al Falahi, 2000). Kashmolah (2003) obtained a statistically significant correlation between the binding energy of the simplified Langmuir equation and calcium carbonate (r = 0.47), which confirms the importance of total calcium carbonate in influencing the adsorption energy of boron (Gupta, 1993).The results of Table (3) showed that the values of the binding energy coefficient (k) for Al-Madina soils and added materials, according to the Langmuir equation, ranged between (0.0025 - 0.0128) ml/µg B, with an average of (0.0078) ml/ µg boron, while the values of (k) increased for Al-Zubair soil, where it ranged between (0.0127 - 0.0158) ml/ µg boron and an average of (0.0145) ml/ µg boron. This value is low compared to what he found Murtadh *et al*(1988) , Alwan(1989) and Al Falahi(2000), It appears from the results of the study that there is a significant effect of the chemical and physical properties of the soil in determining the adsorption of the soil. It can be concluded that the increase in the soil content of mineral colloids (clay and silt) plays a role in the adsorption of boron by the soil. (Keren *et al* ., 1985; Goldberg and Glaubig, 1986, Al-Falahi, 2000, and Kishmolah, 2003). The clay collids play an important role in the adsorption of boron as the fine texture soil are more capable of holding boron compared to the coarse texture soil, as the clay granules have a high ability to hold boron by the broken edges through the substitution between OH^- on the surface and the borate ion.

The results in Table (3) showed that the added materials (zeolite, Biochar, cow manure, and plant residues) differed among themselves in giving values for the adsorption equations constants (qm, k). The values of the correlation coefficient (k) for zeolites and and Biochar are high and compared to other materials (organic wastes), and the values of the maximum adsorption (qm) decreased in coarse texture soils (Al-Zobair) compared to fine tissue soils (Al-Madina), according to the Langmuir equation. This is due to the role of zeolite and biochar in improving soil properties.

Table (3) Langmuir and Freundlich equation constants and correlation coefficient (r) for the materials used in the study soils

Soils	Treatments	The Langmuir equation			The Freundlich equation		
		qm g g^{-1}µ	K_L g^{-1} µml	Simple correlation coefficient (r)	n g g^{-1}µ	K_f g^{-1} ml	Simple correlation coefficient (r)
Al-Zubair	Zeolites	77.519	0.0158	0.9943	1.247	1.6403	0.9975
	Biochar	70.922	0.0148	0.9907	1.220	1.3540	0.9969
	Cows' manure	63.291	0.0145	0.9804	1.214	1.1755	0.9957
	Plant residues	68.493	0.0127	0.9708	2.484	1.1457	0.9963
Al-Madina	Zeolites	136.986	0.0128	0.9775	1.202	2.2841	0.9965
	Biochar	156.250	0.0091	0.9602	1.168	1.8181	0.9997
	Cows' manure	454.545	0.0025	0.9582	1.041	1.2508	0.9997
	Plant residues	192.307	0.0066	0.9534	1.117	1.5233	0.9999

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