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SORPTION OF PHOSPHATE FROM ACIDIC WASTEWATER INTO THREE TUNISIAN CLAY SOILS

The removal of phosphates from acidic wastewater using three soil minerals (Soil1, Soil2, and Soil3) with high content of paligoskite, smectite and illite, respectively, is studied. The effect of the medium pH value, contact duration and solid:liquid ratio is considered. The smectite-containing soil possesses the highest sorption capacity with respect to phosphate. The isotherms of phosphate sorption by soils are processed in the Freundlich and Langmuir equation coordinates. It is shown that the fitting of isotherms in the Freundlich equation coordinates results in better correspondence with experimental data. In addition, the adsorption selectivity of ions (PO_4^{3-}, F^-, Cl^-) existing in waste solution by these soils was studied, and the fluoride is more selective at acidic pH region.

1. Introduction

Phosphate is usually considered as the main factor causing environmental deterioration of water nature. The ability to predict leaching rates of phosphate through soils to groundwater and surface water is therefore essential for the long-term management of a site for land disposal of waste. However, phosphorus removal from wastewater has been widely studied during the past decades by some authors [1 – 4]. Several parameters and typical removal methods such as chemical and biological treatments have been successfully applied [1]. In this context, we can note that the pH and the soil contents of iron, aluminium, calcite and organic matter are factors affecting immobilization of soluble P applied to soil through adsorption and/or precipitation reactions [5, 6]. Furthermore the clay and clay soil was selected among the best natural adsorbent of phosphate [7 – 10]. In addition the presence of calcite in the soil increase the phosphate removal by physical adsorption and precipitation at pH greater than 6 [11,12].

This paper reports phosphate retention/adsorption throughout the profiles of three Tunisian clay soils intended for the storage of an industrial waste. This waste is an acidic aqueous solution of pH 3, where the phosphate concentration is about 1500 mg P/L. An attempt is also made to relate adsorption to physical and chemical characteristics of these soils. Besides, the capacity of phosphate sorption by these clay soils was found to depend on pH solution, solid–liquid ratios and available phosphate concentration with equilibrium being achieved within 1 – 2 days. In addition, the adsorption characteristics of these materials for phosphate removal from aqueous solutions were evaluated in batch experiments and the isotherms were fitted by Langmuir and Freundlich models.

2. Materials and Methods

The natural samples used in the present experiments were obtained from three locations designed for acidic waste disposal in the South-East of Tunisia. However, the purification was made by the classical method of NaCl exchange [13]. Its physico-chemical compositions (determined by chemical analysis and XRD), the cationic exchange capacity (CEC) and specific surface areas (S_{BET}) are presented in Table 1. The initial phosphate content in all samples not exceeds the 0.1% of the hydrated sample. For all samples, the powders was sieved to particle sizes lower than 106 мм and were dried at 90°C for a minimum of 24 hours before sorption studies.

Table 1. Mineralogical composition, CEC and S_{BET} of samples according to Hamdi et al. [14]

Sample	Mineralogical composition of clay samples (%)							S_{BET} (m^2/g)	CEC (meq/100g)
	Paly	Smec	Kao	Il	Q	Ca	Do		
Soil1	35.5	1.7	14.9	–	28	18.9	–	35.4	16.5
Soil2	–	56.3	6.5	–	12.9	25.6	–	57.1	49.8
Soil3	–	–	22.9	62.7	8.8	–	4.7	91.5	24.7

Paly: palygorskite, Smec: Smectite, Kao:Kaolinite, Il: Illite, Q: Quartz, Ca: Calcite, Do: Dolomite

2.1. Instruments for phosphate and pH measurements. The pH measurements were made using an HI 9321 Microprocessor pH meter (HANNA Instruments) combination electrode. Phosphate concentration was measured by the standard method (vanadomolybdophosphoric acid colorimetric method) [15] using the spectrophotometer Hach DR/4000. Adsorbed phosphate was calculated from the difference between the initial phosphate concentration and the concentration of phosphate that remained in the supernatant solution.

2.2. Experimental procedure for sorption studies. Adsorption capacities for the different samples were determined at different pH values range (3 to 9) by shaking 1g of sieved and dried sample with 25 ml of 500 mg_P/L of KH_2PO_4 solution in polyethylene bottles at 25±2°C. Small amounts ($5\cdot10^{-1}$ or $5\cdot10^{-2}$ M) of HNO_3 or NaOH were also added initially to provide the solutions with final pH values, then the solute was made up to a volume of 30 mL with deionised water. The bottles were agitated in a rotary agitator for periods ranging from 1 hour to 2 days before being centrifuged at 3000 rpm for 10 min. After centrifugation, total phosphorous concentrations in the recovered solution were measured.

Phosphate sorption isotherms were determined by a procedure similar to that described above. One gram of sample and 25 mL of KH_2PO_4 solution at various concentrations (50 to 2000 mgP/L) were pH has adjusted to 3±0.2 and the solute was made up to a volume of 30 mL with deionised water, also were mixed in polyethylene bottles at 25±2°C.

3. Results and discussion

3.1. Equilibrium time. Phosphate is adsorbed rapidly at the soil surface and equilibrium is reached within 24 h according Ye et al [7] and Gerritse [12]. This physically adsorbed phosphate on the soil sample surface is termed mobile as it is readily exchangeable. After the initial adsorption to the surface, phosphate continues to react with the soil sample. In this study, the results of phosphate adsorption kinetic experiments at 25±2°C show that the equilibrium is reached within 20 h using a synthetic solution and 48h, using the wastewater. This delay of adsorption in the case of waste solution is caused by the effect of the other ions on the sorption kinetic phenomena. Moreover, this contact time was considered as the equilibrium time for the following adsorption study.

3.2. Effect of pH on phosphate adsorption. With a similar procedure, the effect of pH on phosphate adsorption was examined in a series of experiments that used the same initial phosphate concentration (500 mgP/L) while maintaining pH at different values between 3 and 9. The effect of pH on phosphate adsorption for these soils is illustrated in Figure1 for purified samples and Figure 2 for raw samples. Adsorption of phosphate by purified clay as a function of pH clearly differs from the pH response for the raw sample. Besides, for the pure Soil3 sample the general shape of the pH curves with a peak in adsorption for illite and kaolinite at pH 4 – 6 accords well with the results obtained by other investigators [16,17]. In the case of pure Soil1 the adsorption decreases with pH increasing, whereas in the case of pure Soil2 sample is the contrary. This increased phosphate adsorption can be explained by the fact that smectite contains a large amount of exchangeable calcium that can react with phosphorus to form an insoluble calcium phosphate phase [17, 18]. Furthermore, the results of raw samples show that the phosphate removal increase with increasing pH and the Soil2 have the higher adsorption capacity. This greatest removal efficiency of phosphate occurred at alkaline conditions due to the higher calcium content and/or to the calcite or dolomite fraction.

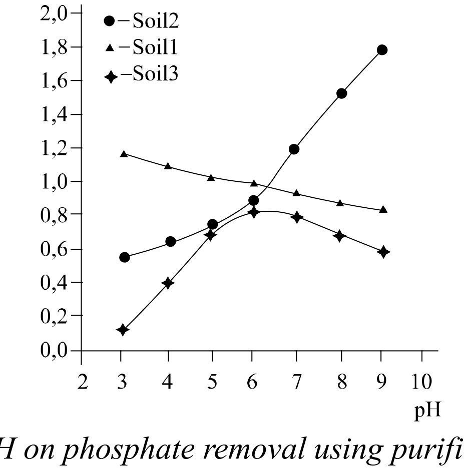

Figure 1. Effect of pH on phosphate removal using purified samples

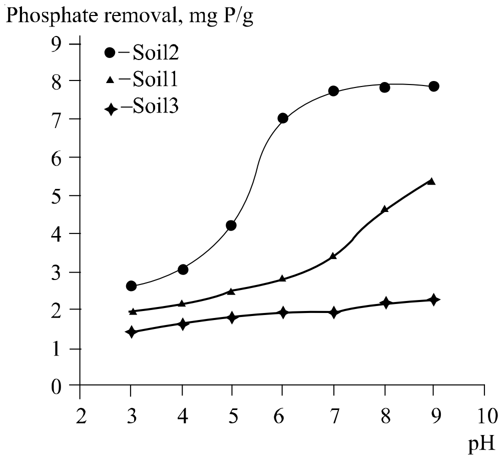

Figure 2. Effect of pH on phosphate removal using natural samples

3.3. Phosphate sorption isotherms. Based on the results of the kinetic studies and in order to work in the same condition of wastewater, all equilibrium experiments were carried out at pH 3±0.2 and for a reaction period of 24 h using KH_2PO_4 solution at various concentrations (50 to 2000 mg P/L). The results of these equilibrium adsorption experiments are presented in Figure 3.

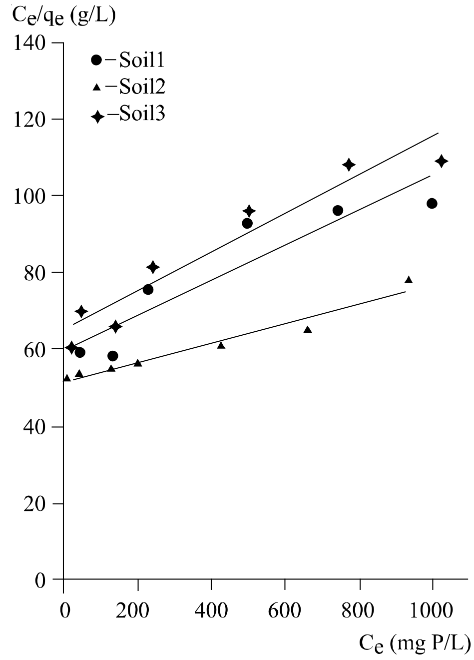

Figure 3. Linearized Langmuir adsorption isotherm of the three samples

The experimental sorption data for the adsorption of phosphorous were correlated with Langmuir (Eq. 1) and Freundlich (Eq. 2) models:

$$q_e = \frac{Q_0 b C_e}{1 + bC_e}\ , \qquad (1)$$

$$q_e = K_F C_e^{1/n}\ . \qquad (2)$$

Where q_e is the amount of ions adsorbed per unit weight of adsorbents (mg/g), C_e is the equilibrium concentration (mg/L), Q_o and b are the Langmuir constants related to capacity and energy of adsorption, respectively. K_F and 1/n are the Freundlich constants. The phosphate adsorption capacity increased with the phosphate equilibrium concentration increasing. However, the theoretical linearized of Langmuir and Freundlich isotherms are plotted in Figures 3 and 4 together with the experimental data points.

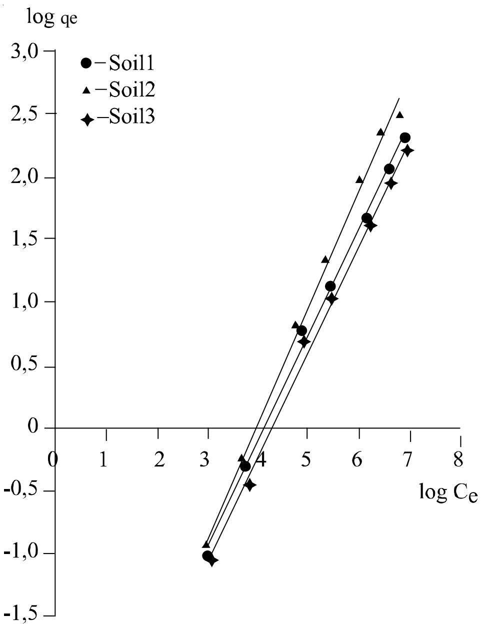

Figure 4. Linearized Freundlich adsorption isotherm of the three samples

The estimated model parameters with the correlation coefficient (R^2) are shown in Table 2. The fitting curves from the two isotherms are also illustrated in Figure 5. It is shown that the experimental data of phosphate adsorption on these samples could be well fitted by the isotherms. We can notes that the samples differ in their capacity to adsorb phosphate and Soil2 adsorbing more than Soil1 which adsorbed more phosphate than Soil3. Clearly, the Freundlich equation provided better fitting in terms of r^2 range between (0.997 – 0.999). The results of Langmuir isotherm shows that the soil2 had higher adsorption capacity of order of 31.84mg/g, this result is slightly higher comparing to literature [7, 17]. This is explained essentially by the highest concentration used in this study and by chemical bonding of the anions to positively charged surfaces at pH 3 on the clays.

Table 2. Summary of optimised isotherm parameters

Samples	Isotherm type					
	Langmuir			Freundlich		
	Q_0 (mg/g)	b (l/mg)	r^2	K_F	1/n	r^2
Soil1	23.31	$6.92\ 10^{-4}$	0.831	0.030	0.84	0.999
Soil2	31.84	$6.18\ 10^{-4}$	0.953	0.029	0.88	0.997
Soil3	19.53	$7.82\ 10^{-4}$	0.894	0.029	0.82	0.998

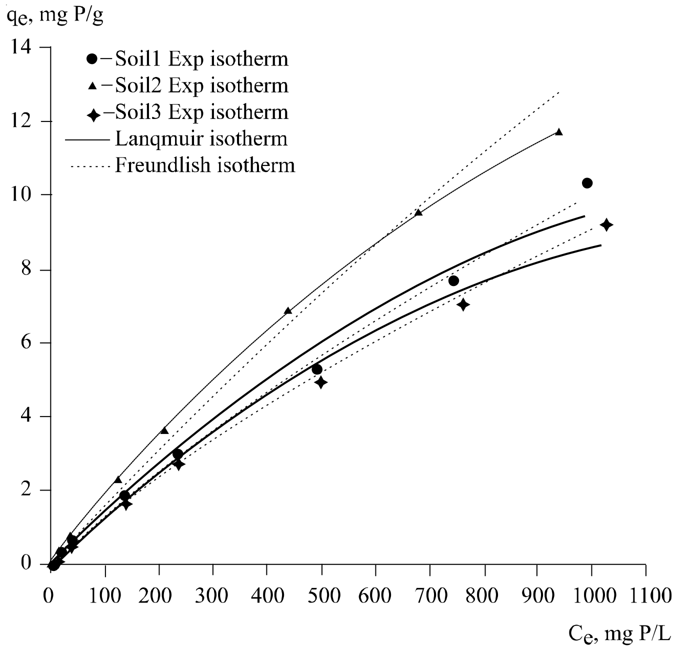

Figure 5. Experimental sorption of phosphate by three samples with fitted Langmuir, and Freundlich isotherms at pH=3±0.2

3.4. Effect of solid-liquid ratios. Some interested studies [13] have shown that both organic and inorganic contaminant sorption is dependent on the solid–

liquid ratio to some degree. However, the S/L ratio presents a significant influence on the sorption behaviour and its increase supports the increasing of adsorption capacity. In this context, we studied here the batch tests of solid–liquid ratios of the magnitude smaller than 3.33%, 6.66% to greater than10% using the lixiviate solution of pH of 3 and phosphate concentration of 1500 mg/L. The determination of separate sorption equilibrium time was performed for these samples. For all sample the equilibrium time necessary for the 6.66% and 10% solid–liquid ratio was needed 2 days minimum. This increase in time was probably caused by particle aggregation and the poorer quality of mixing within the small vials. Also, we noticed that for all samples the adsorption increase with increasing S/L ratios (Figure 6, 7 and 8). This increased phosphate removal can be explained by the augmentation of the pH and by the large amount of calcite that can react with phosphorus and form an insoluble calcium phosphate phase.

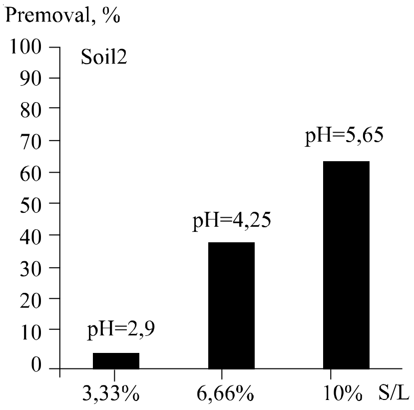

Figure 6. Effect of the solid-liquid ratios on the phosphate removal by Soil2

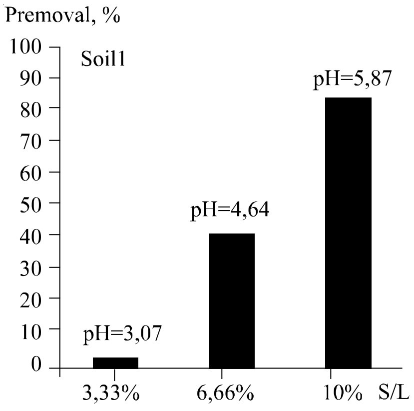

Figure 7. Effect of the solid-liquid ratios on the phosphate removal by Soil1

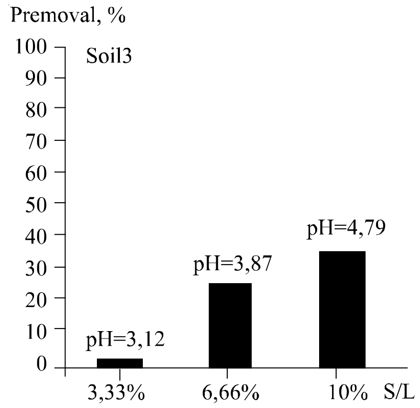

Figure 8. Effect of the solid–liquid ratios on the phosphate removal by Soil3

3.5. Effect of other Anions on phosphate removal. Some investigators have proposed an ion-exchange reaction as a possible mechanism for phosphate adsorption on clay soil. To test this theory, the adsorption of phosphate by Tunisian soils in the presence of wastewater concentrations of F^- and $C1^-$ and at pH=3 was investigated. Table 3 shows that the selectivity of the fluoride adsorption onto three samples was 25 – 50 times greater than phosphate adsorption. The amount of phosphate adsorbed on all sample in waste solutions was less than that in single solutions Figure 9. However, in this waste solution at pH 3 these soils selectively adsorbed fluoride more than phosphate.

Table 3. Selectivity adsorption study of anions (PO_4^{3-}, F^- and Cl^-) from wastewater on three samples

Anions	Anions Initial concentration in wastewater (mg/L)	Removal capacity (mg/g) at pH=3±0.2 and S/L ratio=3.33%		
		Soil2	Soil1	Soil3
F^-	2360	57.04	60.01	51.92
PO_4^{3-}	1500	2.43	1.52	1.12
Cl^-	880	2.17	1.45	0.05

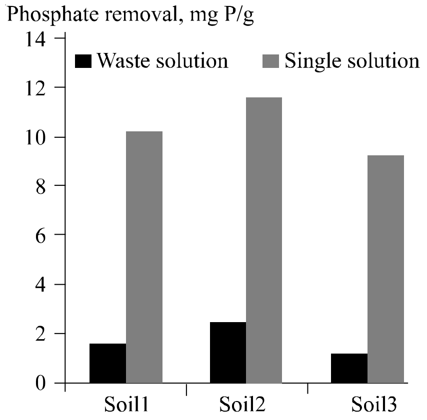

Figure 9. Amount of phosphate removal by three samples from single and waste solution. pH = 3, S/L ratio=3.33% and 1500 mg P/L

4. Conclusions. Three Tunisian natural soils were tested to remove phosphate ions from KH_2PO_4 solution and acidic wastewater. However, kinetics, pH effect, the solid-liquid ratios, and effect of others anions as (F^- and Cl^-) were examined. The results show that for all samples the phosphate removal increase with increasing pH and the Soil2 have the higher adsorption capacity. This greatest removal efficiency of phosphate occurred at alkaline conditions due to the higher calcium content and/or to the calcite or dolomite fraction. The results of the experimental data of phosphate adsorption on these samples could be well fitted by Freundlich isotherm. Furthermore, the solid-liquid ratios play an interested role for phosphate uptake, the maximum of removal capacity was found for S/L ratios of 10%. The amount of phosphate adsorbed on these soils from single and waste solution show that the adsorption is very important in the first case. In addition, the effect of other anions on phosphate adsorption may be due to waste composition, pH and their affinity towards these soils. Moreover, the fluoride is more selective in this waste condition.

Резюме. Вивчено видалення фосфатів з кислих стічних вод трьома видами ґрунтових мінералів (ґрунт 1, ґрунт 2 і ґрунт 3) з високим вмістом палигорскита, смектита і ілліта відповідно. Розглянуто вплив pH середовища, тривалості контакту і відношення кількості твердої речовини до рідини. Ґрунт, що містить смектит має найбільшу сорбційну ємність выдносно фосфату. Ізотерми сорбції фосфату оброблені по рівняннях Фрейндліха і Лэнгмюра. Показано, що представлення ізотерми в координатах Фрейн-дліха краще погоджується з експериментальними даними. Крім того, вивчена селективність адсорбції іонів (PO_4^{3-}, F^-, Cl), що присутні у стічних водах, цими ґрунтами. З’ясовано, що селективність ґрунтів найбільш висока відносно фториду в кислому середовищі

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СОРБЦИЯ ФОСФАТА ИЗ КИСЛЫХ СТОЧНЫХ ВОД ТРЕМЯ ВИДАМИ ТУНИССКИХ ГЛИНИСТЫХ ПОЧВ

Реферат

Изучено удаление фосфатов из кислых сточных вод тремя видами почвенных минералов (почва 1, почва 2 и почва 3) с высоким содержанием соответственно палыгорскита, смектита и иллита . Рассмотрено влияние pH среды, длительности контакта и отношения количества твердого вещества к жидкости. Почва, содержащая смектит, обладает наибольшей сорбционной емкостью по отношению к фосфату. Изотермы сорбции фосфата обработаны по уравнениям Фрейндлиха и Лэнгмюра. Показано, что представление изотерм в координатах Фрейндлиха лучше согласуется с экспериментальными данными. Кроме того, изучена селективность адсорбции ионов (PO_4^{3-}, F^-, Cl), присутствующих в сточных водах, этими почвами. Выяснено, что селективность почв наиболее высока по отношению к фториду в кислой среде.

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