Research Article

Retention of Organic Matter Contained in Industrial Phosphoric Acid Solution by Raw Tunisian Clays: Kinetic Equilibrium Study

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Purification of industrial phosphoric acid (H_3PO_4) is considered a major problem and several methods have been evaluated. In this study, two different types of clay, raw bentonite clay (RBC) and raw grey clay (RGC), were used for removal of SOM contained in H_3PO_4 at low pH. The used samples were characterized by X-ray diffraction, chemical analysis, and specific surface area and MET was also realized. The ability of clay samples to remove S.O.M from aqueous solutions of industrial phosphoric acid has been studied at different operating conditions: temperature, agitation speed, contacting time, and so on. The results indicated that adsorption is an exothermic process for lead S.O.M removal. The equilibrium adsorption data were analysed using the Langmuir and Freundlich isotherms. The results showed that the equilibrium adsorption capacities for the two adsorbents followed best the Langmuir model. Thermodynamic parameters showed that the adsorption process was spontaneous and exothermic.

1. Introduction

The phosphoric acid is manufactured using different processes; the most commonly used area is thermal and wet-process [1, 2]. Phosphoric acid produced by this process contains a variety of impurities, which vary according to the origin of the minerals. Tunisian phosphoric acid (54% P_2O_5) contains about 10 molar impurities per 100 molar H_3PO_4 [3].

The crude acid produced by the wet process is heavily entrained with both mineral (arsenic, cadmium, fluoride, sulfate, copper, and so on) and organic impurities (di-n-butyl phthalate, humic acid, and fulvic acid) [4]. Depending on the industrial phosphoric acid origin and quality, organic matter content is generally between 300 and 700 ppm [5]; these organic impurities affect the acid grade.

Many of these impurities, particularly the solid impurities, are removed from the acid, whatever their uses are, by techniques such as clarification. The presence of these impurities affects the quantity and the quality of the product [6]. For this reason, about 95% of the acid produced by the wet process is directly used as fertilisers and excluded from the use in nonfertiliser applications [7]. Organic matter can

be found both as colloidal suspension and in soluble form [8]. With the aging of H_3PO_4 , the colloidal organics coagulate with the precipitating gypsum, while the soluble organics remain in solution [9]. A great number of research works have been reported in the literature concerning the purification of phosphoric acid and particularly the elimination of the heavy metal cations [10]. However, only few studies are dealing with the removal of organic compound. Most of the adopted processes to achieve this task are mainly based on either liquid-liquid extraction or adsorption on suitably chosen solid supports [11].

Many kinds of adsorbents have been developed for the removal of humic substance (HS) from water. Previous research has suggested that activated carbon, as well as resins, can be reasonably used in order to remove HS from water [12]. Recently the usage of natural mineral sorbents for wastewater treatment is increasing because of their abundance and low price [13] like bentonite clay mineral. Consequently, the purpose of this work is to study the feasibility of OM present in Tunisian wet phosphoric acid elimination onto two different types of Tunisian clays from two different regions. An equilibrium adsorption isotherms' analysis to

FIGURE 1: Spectrum of wavelength of 54% industrial phosphoric acid solution.

obtain the Langmuir and Freundlich constants was realized. A fully Kinetic investigation is also undertaken. Results are compared with those obtained with activated carbon.

2. Materials and Experimental Procedures

2.1. Industrial Phosphoric Acid. Phosphoric acid used in this study is produced by Tunisian Phosphate Mines—GCT complex located in Gabes, South of Tunisia. Qualitative and quantitative analyses of phosphoric acid have already been performed in previous studies [5]. The wet phosphoric acid which we treated initially contains an equal amount to 54.65% P_2O_5 and a quantity of organic matter equal to 491 mg/L. 82% by weight of organic matter consists of humic substance (Figure 1). Figure 2 showed the spectrum scanning wavelength of 54% industrial phosphoric acid solution which confirms that the OM concentration in the clear supernatant at different time intervals can be determined spectrophotometrically at 418 nm [14–16]. The viscosity of phosphoric acid was determined in the temperature range of 16–50°C. The density, viscosity, and the chemical composition of H_3PO_4 were measured with results shown in Table 1.

2.2. Phosphoric Acid Used as Reference. The phosphoric acid used as reference was obtained by continuous stirring at room temperature of phosphoric acid with activated carbon of less than 0.15 mm in size during a whole day. The acid obtained was filtered on paper filter and the above procedure was repeated for five days until the phosphoric acid was OM-free and used as a blank in the UV spectrophotometric analysis [15, 16].

2.3. Bentonite and Gray Clay. In this study, two raw materials were used: bentonite and gray clay which were sampled in Djebel Hamma in Gabes area (Southeast of Tunisia)

TABLE 1: Physical and chemical characteristics of 54% industrial phosphoric acid solution.

Material	H_3PO_4
Organic matter (ppm)	491
P_2O_5 percentage (%)	54.26
Ph	≈ 1
Density	1.6
Al (mg/L)	10470
Ca (mg/L)	4200
Fe (mg/L)	14600
Cd (mg/L)	24.315
Cr (mg/L)	380.2
Viscosity (cPo)	6.34

and Djebel Cherahile, Kairouan-Tunisia (Center of Tunisia), respectively.

2.4. Characterisation Methods. To determine the various chemical species, constituting the clay material, normative mineral composition was calculated from the quantitative chemical analysis obtained by X-ray powder diffractometer (Rigaku D-Max 2200 model). For the loss on the ignition (LOI) determination, the raw clay material was calcined at 1000°C.

To identify the mineralogical composition of the material and the changes of interlayer spacing of the prepared samples, a Philips analytical X-ray diffractometer was used employing filtered Cu radiation generated at 40 kV with a scan rate of 1°/min at room temperature. Bragg's law, defined as $n\lambda = 2d \sin \theta$, was used to compute the crystallographic spacing (d) for the examined clays (where λ corresponds to the wavelength of the X-ray radiation used for the diffraction experiment and θ is the measured diffraction angle).

X-ray diffractograms were obtained on oriented samples. To prepare the oriented films, the clay material was dispersed in distilled water, and after sedimentation; the fractions with particle size smaller than 2 μm were recuperated and deposited on glass slides. Three blades were analyzed: the first was normal, the second was heated at 550°C during 4 h, and the third was exposed to the vapour of ethylene glycol during 24 h [17].

The density of the clay mineral was measured by pycnometry in order to determine the real density ρ_s ; the fluid chosen to penetrate in porous space was water, whereas, for the apparent density, mercury was chosen since it does not penetrate in the porous network [18]; one can also cover the sample by a film with wax and use water like pycnometric fluid. N_2 adsorption isotherms were recorded on a Micromeritics ASAP 2010 gas analyzer. Surface areas were measured by the BET method and the pore size distributions and pore volume were measured by the BJH method. The samples that have particle sizes lower than 100 μm were degassed as a preliminary to 60°C during 72 hours, and then the cell was plunged in a liquid nitrogen balloon. For transmission electron microscopy, micrographs are recorded on an apparatus JEOL JEM-100CXII operating at 200 KeV.

FIGURE 2: X-ray diffraction patterns of (a) RBC and (b) RGC.

To prepare the sample, a few milligrams of clay mineral powder are mixed in a beem capsule with agar 100 embedding resin. After polymerization at 60°C overnight, the blocks are cut using a microtome equipped with a diamond knife. The ultrathin slices, ~50 nm, are recovered on copper grids and examined.

2.5. Organic Matter Removal Test (Experimental Procedure). The industrial phosphoric acid solution used was a 54% P₂O₅ (about 9 M H₃PO₄) solution containing an initial concentration of organic matter (OM) equalizing with 491 ppm. The removal of OM was carried out in the following manner: a known amount of used adsorbents was placed in Erlenmeyer flasks of 250 mL capacity in contact with 50 mL of industrial phosphoric acid solutions at a certain temperature (35–55°C) under variable agitation speed (200–600 rpm) at very acidic pH value. After contact desired time and at equilibrium, the dispersions were filtered, and the OM concentration was determined by spectrophotometry (UV-visible spectrophotometer 1650, SHIMADZU) at a wavelength of 418 nm (Figure 2).

The amount of OM adsorbed was calculated by using the following equation:

$$q_e = \frac{(C_i - C_f)}{M} \times V, \quad (1)$$

where q_e is the amount of OM adsorbed on the clay (mg g⁻¹), C_i is the initial OM concentration in solution (mg L⁻¹), C_f is the final OM concentration in solution (mg L⁻¹), V is the volume (L), and M is the amount of clay (g).

The kinetic study was carried out on the same experimental setup by varying one parameter and keeping the others constant.

3. Results and Discussion

3.1. Characterisation of the Adsorbent. The RBC sample contains smectite (bentonite) as the major clay mineral associated with illite and kaolinite; this clay mineral was characterized by the (0 0 1) basal reflections at 14.7 Å, 10.04 and 7.17 Å [17] on rock powders (Figure 2(a)). The RGC sample contains illite as major clay minerals (Figure 2(b)). The diffraction characteristics of quartz and calcite appear clearly on XRD patterns of RGC.

TEM micrographs (Figures 3(a) and 3(b)) of the raw used clay show a (001) reflexion corresponding to 1.46 and 0.95 nm, respectively. This result is in agreement with the value obtained by XRD. So the TEM observation of the two samples RBC and RGC supports RX results found previously.

The chemical analysis showed that the main constituents of raw clay materials (RBC and RGC) are silica, alumina, iron, calcium (RGC), and magnesium (RBC) oxides (Table 2). The absence of correlation between SiO₂ and Al₂O₃ contents indicates that the excess of SiO₂ is due to the presence of quartz, as shown by XRD. RBC sample has higher content of MgO (3%) than the RGC sample (1.2%) (Table 2); such difference is explained by the occurrence of smectite amounts.

Textural analysis of the RBC and RGC adsorbents is given in Table 3. By comparison with RGC sample, it is clear that the RBC sample has a higher specific surface area, total pore volume, internal porosity and pore size. Moreover, RBC is more porous than RGC.

TABLE 2: Chemical characteristics of raw clays (in mass %).

Oxides %	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	MnO	ZnO	CaCO ₃	LOI
RGC	43.38	16.82	8.67	0.86	3.46	0.53	0.05	0.12	7.10	8.56
RBC	50.91	16.59	10.56	0.96	1.2	1.85	0.04	0.19	3.02	11.2

LOI: loss ignitions; RBC: raw bentonite clay; RGC: raw gray clay.

FIGURE 3: TEM observations of RBC (a) and RGC (b).

TABLE 3: Textural analysis of samples.

Parameters	RGC	RBC
Real volumic mass ρ_s (g/cm ³)	2.58	2.18
Apparent volumic mass ρ_p (g/cm ³)	1.87	1.38
Internal porosity χ (%)	27.77	36.69
Specific surface S_{BET} (m ² /g)	36.00	56.47

As shown in Table 3, the Specific Surface area S_{BET} of RBC is 56.47 m²/g, which is much larger than that of RGC. This confirms the XRD and MET results.

3.2. Effect of the Physicochemical Parameters on the Retention of OM onto Used Adsorbents

3.2.1. Effect of Contact Time. The time-dependent behaviour of lead adsorption was studied by varying the contact time between the SOM and adsorbent in the range of 1–120 min. The initial concentration of OM was kept as 491 ppm, while the dose of RBC and RGC samples was 1 g. The data showed that the sorption of lead OM on the two studied clay samples was fast and the equilibrium was reached after 90 min (Figure 4). The adsorption process is fast at the beginning of the reaction due to the adsorption of OM on the surface sites of clay, and then it becomes slow due to the diffusion of OM from the surface sites to the interlayer of the solid [16, 19]. Therefore, a 90 min contact time was found to be appropriate for maximum adsorption and was used in all subsequent measurements.

3.2.2. The Temperature Effect. To examine the temperature effect on the OM retention, the same conditions were

FIGURE 4: Effect of shaking time on retention of OM present in phosphoric acid using (a) RBC and (b) RGC; (Particle size: 63 μ m; C_0 = 491 ppm; S/L = 20 g/L; T : 35°C).

kept while varying the temperature. According to Figure 5, when the temperature increases, the OM adsorption capacity decreases and the OM retention reaches its maximum at 35°C; which would be due to an increase in desorption at high temperature [18] confirming that adsorption is an exothermic phenomenon. Figure 5 confirms the fact that adsorption is physical: the adsorption rate is improved when T° decrease [15, 16]. For the three investigated temperatures, equilibrium is reached after 90 min.

FIGURE 5: Effect of Temperature on OM retention using: (a) RBC and (b) RGC; (Particle size: $63\ \mu\text{m}$; $C_0 = 491\ \text{ppm}$; $S/L = 20\ \text{g/L}$).

FIGURE 6: Effect of particle size on retention of OM using (a) RBC and (b) RGC ($C_0 = 491\ \text{ppm}$; PS = $63\ \mu\text{m}$; $S/L = 20\ \text{g/L}$, $T^\circ = 35^\circ\text{C}$).

3.2.3. Effect of Particle Size. Three particle sizes were used: 63, 125, and $200\ \mu\text{m}$. Figure 6 shows that the rate of adsorption slightly improves when the particle size decreases. This is due to the fact that the surface area increases slightly with decreasing particle size.

3.3. Retention of Organic Matter Contained in Industrial Phosphoric Acid. In our case, the industrial phosphoric acid presented a high solute concentration in the form of minerals so it has a high ionic strength (Table 1). It was noted that the adsorption depends on ionic strength and may be explained by several mechanisms.

- (1) In high ionic strength condition a decrease of molecular volume of humic substance can be noticed due to

minimization of the electrostatic repulsion between ionized oxygen groups, which facilitates the adsorption.

- (2) In high ionic strength condition, a compression of the thickness of the diffuse double layer which surrounds solid and liquid phases when they are in contact, is possible. Such compression helps the clay particles and humic substance molecules to approach each other more closely.
- (3) In addition, at higher ionic strength, the solubility of humic substance is lower, a fact that favors the mass transfer of humic substance from the solution phase to the solid phase of clay [19–21].

TABLE 4: Isotherm constants of O.M adsorption onto RBC and RGC samples at 35°C (particle size: 63 μm ; $C_0 = 491$ ppm; $S/L = 20$ g/L; T : 35°C).

Adsorbents	Langmuir equation			Freundlich equation		
	q_m (mg/g)	K_L (L/mg) 10^3	R^2	$\ln K_F$	$1/n$	R^2
RBC	17.26	3.0	0.994	-31.12	13.06	0.882
RGC	15.05	3.5	0.984	-42.32	14.32	0.963

3.4. Adsorption Isotherms Models. To describe the adsorption process of OM contained in industrial phosphoric acid onto the two considered solid supports (RBC and RGC), two empirical models are tested, which are the Langmuir and the Freundlich isotherms. These two models are generally reliable in modeling the adsorption of inorganic and organic matter in solutions.

The Langmuir and Freundlich models are the simplest and the most commonly used isotherms to represent the adsorption of components from a liquid phase onto a solid phase [22]. The OM adsorption experiment isotherms were carried out at temperature of 35°C by varying the time in the ranges previously defined (in chemical solutions). All other parameters were kept constant. The obtained equilibrium adsorption data were fitted on the linearly transformed Langmuir and Freundlich equations.

Langmuir model assumes a monolayer adsorption. The obtained adsorption data were fitted by the linearized Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}. \quad (2)$$

Both q_m and K_L could be determined from the slope and intercept of the linear plot C_e/q_e against C_e , respectively. C_e is the equilibrium concentration of OM (milligrams per litre), q_e is the adsorbed amount of OM (milligrams per gram), q_m (milligrams per gram) is the maximum adsorption capacity, and K_L is the Langmuir constant related to the adsorption energy [23].

The parameters derived from the least-square fitting of the isotherms by the linearized Langmuir equation (Figure 7) are given in Table 4.

In Table 4, we brought different values of K_L , R_2 and q_m obtained at 35°C.

The monolayer capacity (q_m) for RBC and RGC was 14 and 18 $\text{mg}\cdot\text{g}^{-1}$, respectively.

The main characteristics of the Langmuir isotherm can be also expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which was defined as:

$$R_L = \frac{1}{1 + K_L C_0}, \quad (3)$$

where C_0 is the initial OM concentration. The R_L value indicates the shape of the isotherm as follows: favourable adsorption is indicated by $0 < R_L < 1$ while $R_L > 1$, $R_L = 1$, and $R_L = 0$ describe, respectively, unfavourable, linear, and irreversible adsorption [24]. The R_L values calculated for OM initial concentration of 491 ppm were 0.0033 and 0.0028 at

FIGURE 7: Langmuir equilibrium isotherms of OM adsorbed onto RBC and RGC.

35°C for RGC and RBC, respectively. Hence, the adsorption of OM on RBC and RGC was favourable.

The linearized Freundlich equation was expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (4)$$

where K_F and $1/n$ are constant and considered as indicators of adsorption intensity. The derived parameters from least-square fittings of the Langmuir and Freundlich equations are given, respectively, in Table 4. Freundlich constants, K_F and $1/n$, were determined from the linear plot of $\log q_e$ versus $\log C_e$ (Figure 8).

The correlation coefficients (R^2) given in Table 4 show that the Langmuir equation gives a fairly good fit to the sorption isotherm.

The used bentonite clay, being a polar adsorbent, preferably adsorbs polar molecules [25]. The Langmuir isotherm was characterized by a rise in the adsorption capacity. This can be explained by the penetration of the OM in the macro- and micropores of the adsorbent, forming new adsorption surfaces or by the formation of multilayers as a result of the interactions between the OM and adsorbate [16].

Results in Table 3 show that the maximum adsorption capacity values, Q_0 , are 17 mg/g for RBC and 15 for RGC at a temperature of 35°C and optimum conditions. The observed maximum sorption capacity of RGC for OM removal remained slightly lower compared to maximum

TABLE 5: Thermodynamic parameters.

		308 K	318 K	328 K	$-\Delta H^\circ$ (KJ mol ⁻¹)	$-\Delta S^\circ$ (KJ mol ⁻¹ K)
RBC	$-\Delta G^\circ$	11.41	11.63	11.72	13.26	0.083
RGC	$-\Delta G^\circ$	11.26	11.41	11.47	15.4	0.081

FIGURE 8: Logarithmic plot of Freundlich equilibrium isotherms of OM absorbed onto RBC and RGC.

sorption capacities of RBC which confirm the results found previously.

3.5. Thermodynamic Parameters of Adsorption. To evaluate the nature of adsorption of OM contained in industrial phosphoric acid onto raw studied clays, the removal process was analysed in terms of thermodynamic behaviour. To achieve this goal, three thermodynamic parameters, including free energy (ΔG°), enthalpy (ΔH°) and entropy change (ΔS°), and distribution coefficient K_d [26], were determined by the following equation:

$$\Delta G^\circ = -RT \ln K_L, \quad (5)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT},$$

where T (kelvin) is the temperature and R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the universal gas constant. The values of ΔH° and ΔS° were determined from the slopes and intercepts of the plots of $\ln K_L$ versus $1/T$ [27] (Figure 9). The calculated thermodynamic parameters indicated that ΔH° values were -13.26 and $-15.4 \text{ kJ mol}^{-1}$ for RBC and RGC, respectively (Table 5).

According to Table 4, the negative values obtained for ΔG° indicated the spontaneous nature of adsorption (Table 5). The data of ΔH° and ΔS° values of OM adsorption on the studied samples indicated that adsorption phenomenon is exothermic [28, 29].

FIGURE 9: Relationship between $1/T$ and $\ln K_d$ for the adsorption of OM on the studied samples ($V_{\text{Speed}} = 200 \text{ r/min}$; $C_0 = 491 \text{ ppm}$; $S/L = 20 \text{ g/L}$; $T: 35^\circ \text{C}$).

3.6. Comparison of Capacity Adsorption with Activated Carbon. Figure 10 shows that the adsorption capacity of activated carbon towards OM was better than the two other adsorbents (RBC and RGC) due to its high specific surface area, total pore volume, and internal structure ($1000 \text{ m}^2 \text{ g}^{-1}$). The clay can undergo further treatment (by pillaring another inorganic or organic compound) to change its internal structure while following its internal texture so that it approximates texture of coal to have a good adsorption capacity.

4. Conclusions

From the above study, it may be concluded that the adsorption characteristic has been examined with the variations in the parameters of contact time, agitation speed, and temperature. The most efficient OM adsorption is that obtained under the following optimal conditions: temperature (35°C); solid/liquid ratio ($r = 20 \text{ g/L}$); agitation speed ($V = 400 \text{ rpm}$); shaking time: 90 min. The removal efficiency of two different clay samples illite and smectite was found to be 14 and 18 mg/g, respectively, at optimum conditions. The equilibrium data could be described by the Langmuir and Freundlich isotherm equations, and the Langmuir model appears better to represent the adsorption process than the Freundlich model. In this work, the ΔH° and ΔS° values of OM adsorption on the studied samples indicated that adsorption phenomenon is exothermic. The negative value of ΔG° confirms the feasibility of the retention process as well as its spontaneity. The comparison between OM adsorption capacities of used raw clay materials showed the efficiency of

FIGURE 10: Evolution of the retention rate of OM by different adsorbents ($T = 35^{\circ}\text{C}$; $V_{\text{Speed}} = 200 \text{ r/min}$; $C_0 \text{ (O.M)} = 491 \text{ ppm}$; amount clay: 10 g L^{-1}).

bentonite clay in purification of industrial phosphoric acid in significant amount. The clay can undergo further treatment (by pillaring another inorganic or organic compound) to change its internal structure while following its internal texture so that it approximates texture of coal to have a good adsorption capacity.

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