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Elimination of Acid Red 88 by Waste Product from the Phosphate Industry: Batch Design and Regeneration

Khaled Boughzala and Mustapha Hidouri

Abstract

Waste regenerated after washing of rock phosphate and phosphogypsum has been proposed as removal agents of Acid Red 88 (AR 88) from artificially contaminated solution. Natural phosphate (PN) was also studied for comparison. These materials were characterized beforehand, as is intended for the removal tests, by chemical analysis, powder X-ray diffraction, Fourier-transform infrared spectroscopy, thermogravimetric analysis– differential thermal analysis, scanning electron microscopy, and N₂ adsorption isotherms. The conducted experiments show that among the different materials, the PWR has the highest retention capacity of the dye (123.4 mg g⁻¹) of AR-88. Upon calcinations, the removal capacities reduced by 60 to 70%. We take note also that a decrease in the amount of removed AR 88 dye occurs with an increase in pH. The kinetics data on the reaction between AR 88 and the materials are described well by a pseudo -second-order model. The Langmuir model is successfully applied to the experimental data of the removal of acid red 88. The removal process is exothermic.

Keywords: Natural phosphate, Phosphogypsum removal, Acidic Red 88

1. Introduction

Synthetic dyes have been used in several industrial sectors such as the automotive sector, the textile industries, leather tanning, plastics, aper, and photoelectrochemical cells and therefore, A significant amount of water is used [1]. Wastewater laden with dyes is usually dumped in sewers, rivers, and nearby lagoons. Such treatment affects the water quality, the aquatic ecosystem and the biodiversity of the environment [2, 3]. Wastewater treatment is necessary before it is released into the environment [4]. Likewise, wastewater treatment has been proposed as a solution to obtain good quality water for agricultural and industrial applications [5, 6]. The literature reports several techniques for the treatment and depollution of textiles effluents. It is important to mention, among them, the membrane filtration techniques [7], coagulation / flocculation [8], electro- coagulation [9], oxidation techniques [10] and aerobic biological processes and anaerobes [11, 12]. The search for other effective methods is necessary because these previously described processes have financial limitations and design complexities.

The adsorption process is used for water treatment, however, the high price of adsorbent materials, remains a constraint [13, 14].

Among the proposed solutions include using adsorbents from agricultural residues, for example, the waste material of corn cob, palm fruit parts, the chestnut peel, almond shell, rice husk, orange, and lime peels, pine fruit shells, and others [15, 16].

The clay minerals and the waste produced by the phosphate industries have been used for the retention of textiles dyes [16–21]. The phosphate rocks in Tunisia is considered among the top countries that produce phosphate rocks [22]. Tunisia is ranked among the top phosphate-producing countries. The Natural phosphate (NP) is an abundant product extracted from phosphate rocks and made up of a carbonated fluoroapatite with important substitution of phosphate by carbonate [23]. The literature reveals the existence of a few studies related to the adsorption of some dyes in polluted textile water or adsorption of basic dyes and reactive dyes using natural phosphates (NP) [24–26].

The calcination (heat treatment) of natural phosphate rocks was described in the literature for upgrading the calcareous phosphate ores [27], and to propose other applications than direct synthesis of fertilizers, such the production of pure chemicals, soft drinks and pharmaceutical products [28].

Although the properties of the calcined materials were well documented for the synthesis of fertilizers, however, there are no attempts to describe their usage for the elimination of dyes from polluted water.

Also, the phosphate rocks are converted into phosphoric acid by the addition of sulfuric acid through the so-called wet process [29]. The production of phosphoric acid resulted in the formation of huge amount of wastes by products such as phosphogypsum [30]. Some evaluation of these wastes were proposed in the treatment of polluted water and some research activities have studied their utility as removal agents of some dyes and heavy metal ions from aqueous solutions [31–40].

2. Materials and methods

2.1 Adsorbents

The NP was picked up in the Gafsa-Metlaoui basin (appointed the NP sample). PG is a by-product result of the reaction of sulfuric acid and phosphate rock. PWR is a byproduct of a phosphate company's washing plant. The samples were washed and then heated in an oven at 105° C. The acid dye AR 88 was purchased from ATUL Limited, India; The maximum absorption of this dye is examined at the wavelength of 508 nm. $\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ and oxone (2KHSO_5 KHSO_4 K_2SO_4) were used without further treatment after purchase from Alfa Aesar (4.7% active oxygen) (Alfa Aesar, Lancashire, UK United).

2.2 Adsorption experiments

Different solutions with concentrations between 5 and 200 mg L⁻¹ was prepared by diluting a solution of an initial concentration of 1000 mg L⁻¹. Then, a mass of 0.1 g of the adsorbent was introduced to get to a total volume of 200 mL (dye solution) with a shaking speed equal to 150 rpm, natural pH, and room temperature. The retained quantity (q_e , mg g⁻¹) and the removal percentage (% R) were calculated by Eqs. (1) and (2), respectively.

$$q_t = (C_0 - C_t) \frac{V}{m} \quad (1)$$

$$P(\%) = 100 * \frac{(C_0 - C_t)}{C_0} \quad (2)$$

where C_i and C_e correspond to the initial and equilibrium concentrations of the anionic dye (mg L^{-1}). V is the employed solution volume (L) and m is the adsorbent mass (mg). For to examine the effect of various parameters on the retention of the AR 88 dye, the dosage of adsorbents, kinetic, initial dye concentrations, pH, and temperature were studied independently.

2.3 Regeneration of used materials

NP, PG, or PWR samples were mixed to 200 mL of a fresh solution of AR 88 ($C_i = 200 \text{ mg L}^{-1}$). The mixture is left for 24 hours. The spent adsorbent was obtained by centrifugation and treated with a 10 mL solution of $\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ and 12 mg of oxone ($2\text{KHSO}_5 \times \text{KHSO}_4 \times \text{K}_2\text{SO}_4$). The regenerated adsorbent was centrifuged, washed a few times with deionized water, and then reused in the next run. The solution of Co and oxone was not discharged and used in the next recycle runs [26].

2.4 Characterization

The chemical composition of the used products was determined using atomic absorption spectroscopy (Perkin-Elmer 3110, Waltham, Massachusetts USA).

X-ray diffraction (XRD) patterns were carried on a X'Pert Pro, PANalytical diffractometer (Malvern, United Kingdom) with Cu K radiation.

The data were collected in a 2θ range from 5° to 80° , with a step size of 0.02° and a scanning step time of 10 s. The mineral phases were identified from the data given in the American Society for Testing and Materials cards. FTIR spectra were recorded with a Perkin Elmer 1283 spectrometer (Waltham, Massachusetts USA) in the range of $3500\text{--}350 \text{ cm}^{-1}$ using samples pressed into pellets with KBr.

Thermal analysis was conducted in air from room temperature to 1000°C at a heating rate of $10^\circ/\text{min}$, using a a Setaram Instrumentation (Caluire - France) SETSYS. The surface morphology of the materials was observed by scanning electron microscopy (SEM, FEI Quanta 200, Hillsboro, Oregon, USA). The specific surface area values were estimated from nitrogen adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation. The isotherms were determined using a Micromeritics ASAP 2020 system (Norcross, Georgia, USA). The compounds were outgassed at 120°C for 8 h prior to the measurement. The pH_{zpc} of the NP, PG, and PWR samples was measured in solutions of NaCl (0.01 mol L^{-1}). The concentration of AR 88 at equilibrium was measured during the removal by a UV–visible spectrophotometer (Perkin- Elmer model LAMBDA20, Waltham, Massachusetts USA) at maximum wavelength of 508 nm.

3. Results and discussion

3.1 Characterization of used materials

The values of the chemical analysis are presented in **Table 1**. It is It is remarked that the high CaO concentration (45%) is observed in natural phosphate (NP) compound and it diminished at 26.7% in the phosphate waste rock compound

Samples	%P ₂ O ₅ (%)	CaO (%)	MgO (%)	Cd (ppm)	CaO/P ₂ O ₅
NP	25.64	44.94	0.87	45	1.75
PG	4.06	36.68	0.53	15	0.34
PWR	14.01	26.72	2.15	51	1.90

Table 1.

The chemical analysis of the main elements in the three samples.

(PWR). The NP sample has a the maximum value of P₂O₅ content (25.6%) compared to PWR compound (14.0%).

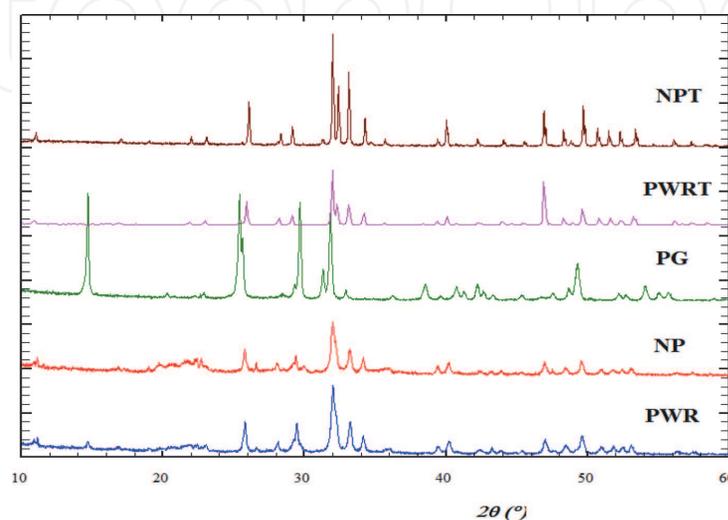
The concentration of anhydride phosphorus pentoxide in NP was close to that reported for similar rocks [33, 34]. The diminish of CaO and P₂O₅ contents was related to washing process. A small percentage of MgO, from 0.87% to 2.15%, was observed. The Ca/P atomic ratio is about 1.75 for NP sample, and close 1.91 for PWR [41, 42]. This variation was due to lower amount of P₂O₅ in PWR, resulted from the washing process. The Cd quantity is located between 45 and 51 ppm [43].

Figure 1 shows the powder XRD patterns of the phosphate waste rock, phosphogypsum, and phosphate waste rock samples. The natural phosphate and phosphate waste rock patterns exhibit similar patterns. Mineralogical identification reveals the presence of carbonate fluorapatite $\text{Ca}_{9.55}(\text{PO}_4)_{4.96}\text{F}_{1.96}(\text{CO}_3)_{1.28}$ and other materials, such as heulandite $((\text{C}_2\text{H}_5)\text{NH}_3)_{7.85}(\text{Al}_{8.7}\text{Si}_{27.3})\text{O}_{72}(\text{H}_2\text{O})_{6.92}$ and quartz (SiO_2) [34]. The sample of phosphogypsum exhibits different phases, such as bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) and anhydrite (CaSO_4) compounds.

The IR absorption spectra of the different samples are displayed in **Figure 2**. The samples present the absorption bands associated to the PO_4^{3-} groups between 1042, 570, 520 and 470 cm^{-1} . These frequencies correspond to the vibration modes ν_3 , ν_4 , and ν_2 , respectively [44].

The FTIR spectrum of the phosphogypsum is shown in **Figure 2**. The spectrum is identified by the typical absorption bands reported for the gypsums compounds [45]. These bands were observed at 1120 cm^{-1} , 600–660 cm^{-1} (ν_4), and 470 cm^{-1} (ν_2).

The doublet at 1463 and 1426 cm^{-1} , and the band at about 863 cm^{-1} were assigned to the ν_3 and ν_2 vibration modes of CO_3^{2-} groups [46]. These bands indicate the existence of CO_3 groups in the gypsum structure. The bands characterized to SiO_2 products are similar to the bands of PO_4 groups at 1042 cm^{-1} , with

**Figure 1.**

Powder XRD patterns of (a) natural phosphate, (b) phosphogypsum and (c) phosphate waste rock. (A) corresponds to anhydrite, (B) to bassanite, (H) to heulandite.

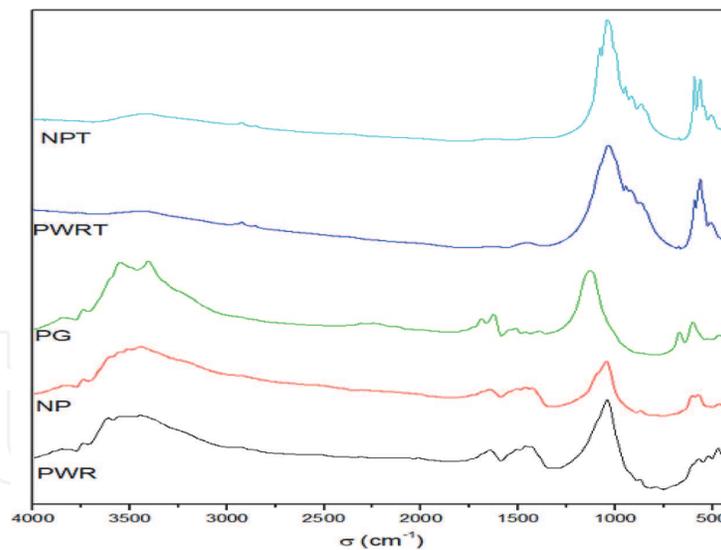


Figure 2.
FTIR spectra of (a) natural phosphate, (b) phosphogypsum, and (c) phosphate waste rock.

a shoulder at 474 cm^{-1} . The bands assigned to adsorbed water molecules at 3600 and 1600 cm^{-1} are present on some spectra.

The thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the natural phosphate and phosphate waste rock samples are given in **Figure 3**. The TGA curve of the natural phosphate and phosphate waste rock samples exhibits three consecutive mass losses. The first mass loss, observed between room temperature and 150°C , is related to the water desorption.

The second mass loss step related to the loss of water content and dehydroxylation from 170 – 450°C . The third mass loss starts at 400°C and continues to $1,000^\circ\text{C}$, is attributed to the decomposition of carbonates and other materials [47]. The two first mass losses are associated with endothermic effects that is observed on the differential thermal analysis (DTA) curve at 85°C , 100°C , 140°C , and 350°C [48]. The Third loss mass is accompanied by two broad exothermal peaks are observed in the range of 700 – 750°C and are attributed to the phase transformation of some resulting samples.

TG/DTA curves of the phosphogypsum product are given in **Figure 3**. The first weight loss observed between 120°C and 350°C is due to the elimination of the entire water of crystallization. The second weight loss achieved between 300°C and 450°C was attributed to the decomposition of CaSO_4 to CaO [49].

The elimination of the entire water of crystallization is related to an endothermal peak at 207°C . The DTA curve exhibits also a broad peak with low intensity.

The scanning electron microscope micrographs of the natural phosphate and phosphate waste rock samples show the presence of nonporous particles of different sizes with spherical shapes or ovoid grains. Also, for the phosphogypsum product, several shapes, such as hexagonal, tabular, and needle-like, are examined (**Figure 4**).

The specific surface areas (SBET) of the three compounds samples are 16.39 , 11.35 , and $26.02\text{ m}^2\text{ g}^{-1}$, respectively, and reveal the nonporous character of these adsorbents.

The slight rise in the SBET value of the phosphate waste rock compound could be interpreted by the acid activation of these rocks.

These values are near to those studied in the case of natural phosphate rocks [50]. The average pore volumes are varied between 0.023 – 0.053 cc g^{-1} . The average pore diameter is in the interval of $[9.58$ – $7.62]$ nm, which proves the nonporous character of the studied samples (**Table 2**).

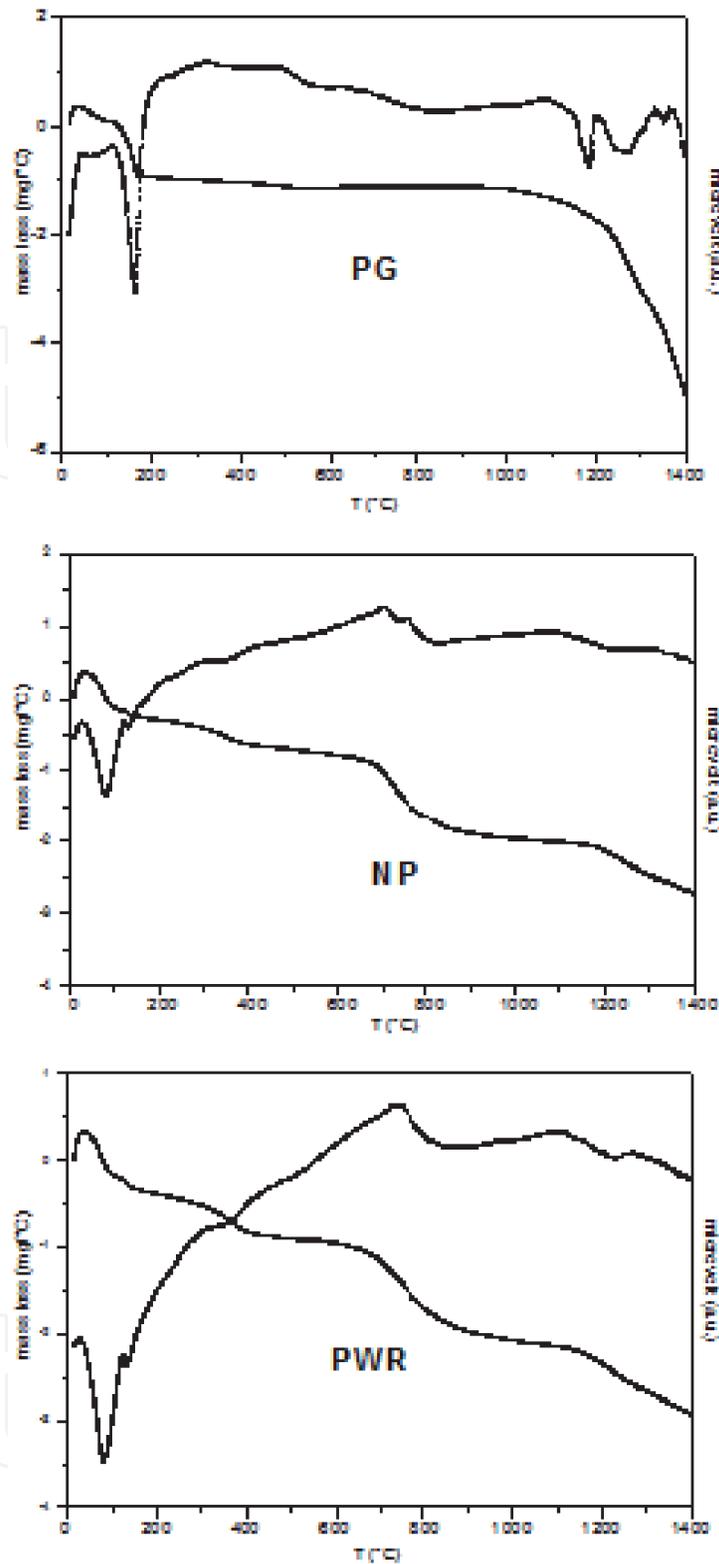


Figure 3. TGA and (A) DTA features of phosphate waste rock. (PWR) natural phosphate, (NP) and phosphogypsum, (PG).

3.2 Removal studies

3.2.1 Effects of solid dosage

A series of runs were carried out by varying the used solid mass from 0.05 to 2 g in 200 mL of AR 88 solution (C_i of 20 mg L^{-1}). The removal efficiency (%) of natural phosphate, phosphogypsum, and phosphate waste rock on the removal of

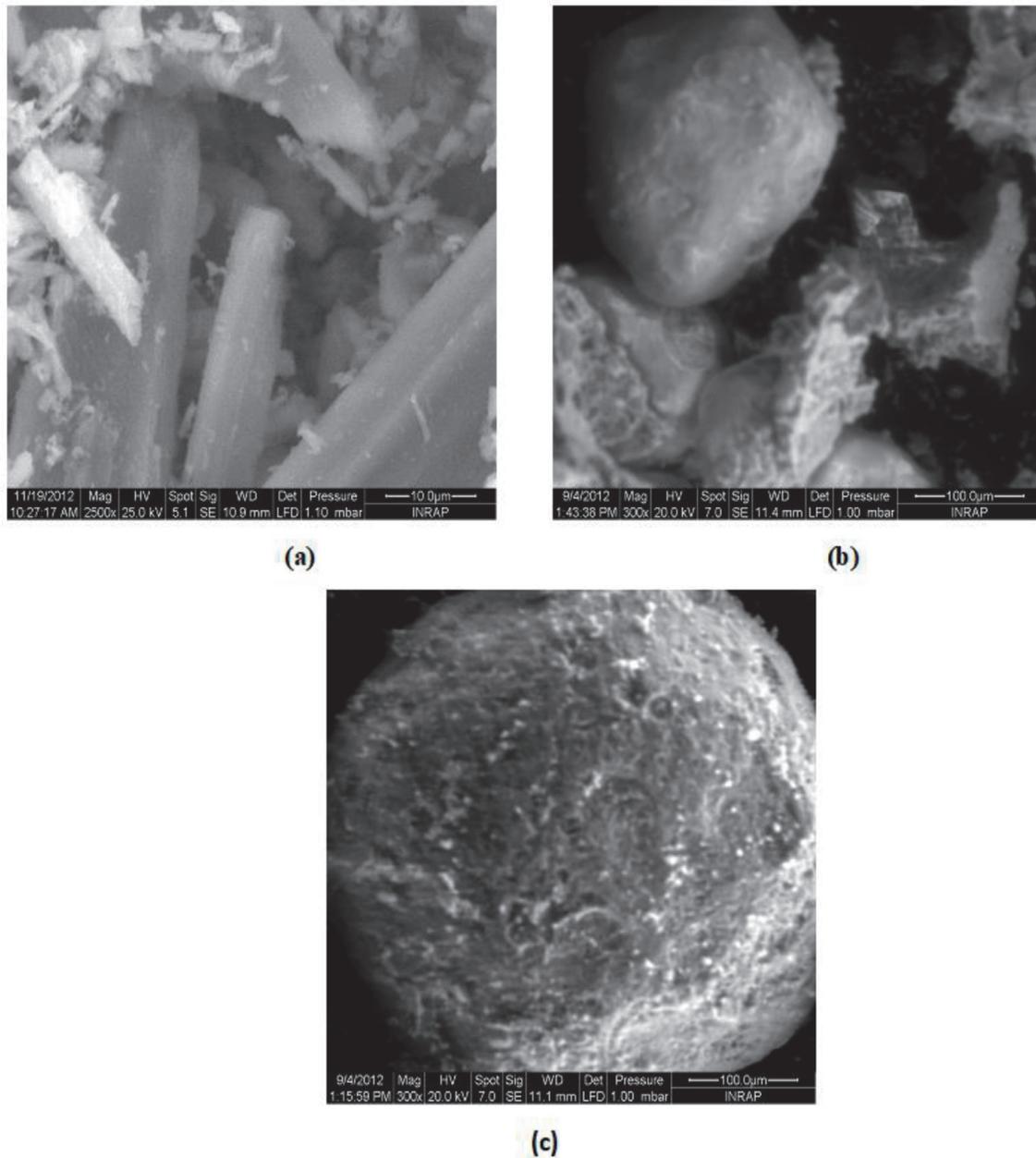


Figure 4. SEM micrographs of (a) phosphogypsum (b), natural phosphate, and (c) phosphate waste rock.

Samples	S_{BET} (m^2/g)	T.P.V (cc/g)	A.P.D. (nm)
NP	11.35	0.027	9.58
PG	16.00	0.031	7.65
PWR	26.43	0.052	7.62

T.P.V = total pore volume; A.P.D. average pore diameter.

Table 2. Micro textural properties of the different materials.

AR88 dye improves as the amount of added solid increases; this is due to the greater availability of active sites on the solid's surface (Figure 5) [51]. In particular, the phosphate waste rock on the removal of AR88 dye material exhibits a significant increase in both dyes removal efficiency, who reached 99% when the mass of used phosphate waste rock on the removal of AR88 dye is 1 g, However, the natural

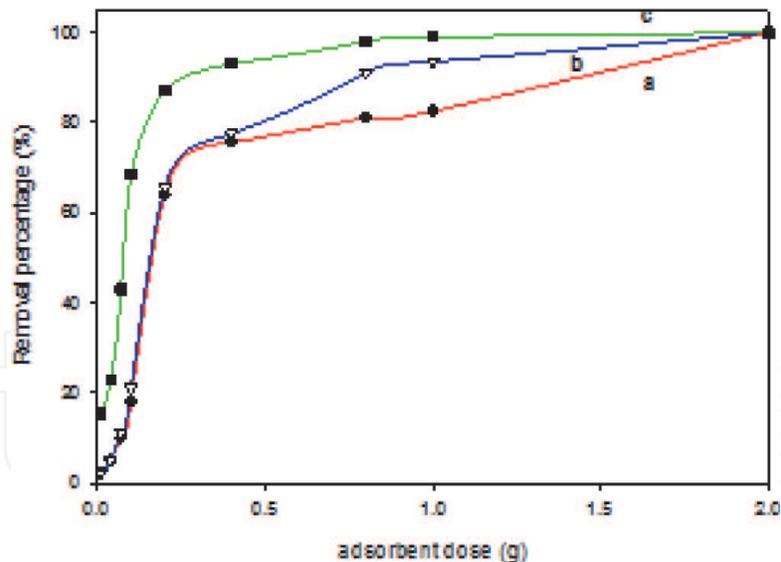


Figure 5.

Effect of dosage mass of (a) natural phosphate, (b) phosphogypsum, and (c) phosphate waste rock on the removal of AR88 dye.

phosphate and phosphogypsum materials exhibit similar removal efficiencies (99%) using a dose of 2 g due to their low removal capacities compared with phosphate waste rock. In general, increasing the removal dosage enhances the removal efficiency the dyes and attributed to the increase of the number of available removal sites.

3.2.2 Effect of pH

The work of the pH was studied at room temperature. The first step consists of a mixture of 1 g of the three adsorbents to 200 mL of AR 88 solution (C_i of 100 mg L^{-1}). In the second step the mixture was stirred for 240 minutes. The pH was altered between 2.5 and 11 using HCl (0.1 M) or NaOH (0.1 M) solutions.

The pH follow-ups the structure of the adsorbates and regulates the charge distribution of the samples [52], the zero-charge point (pzc) was determined first. The point of zero charge (pzc) of the three products NP, PG, and PWR is 6.89, 8.26, and 9.58, respectively. The results revealed that the surface particles are positively charged at pH values below pH_{pzc} , while at pH values lower than pH_{pzc} they become negatively charged.

When the pH diminishes the quantity of acid dye retained by the three adsorbents rises (**Figure 6**). This result can be explained by the dye structure and the protonation of the solid surface [53]. At acidic medium ($\text{pH} = 3$), it exists important electrostatic attractions between the $\phi\text{-SO}_3^-$ groups of the positive surface charges of adsorbents and the dye molecules. Also, the OH^- anions additional are disposable and dispute with the anionic dye for available at higher pH values.

3.2.3 Kinetics of adsorption

The effect of contact time on the retention AR 88 respectively are showed in **Figure 7**. An amount of 1 g of the three samples was added to a volume of 200 mL of a 100 mg L^{-1} dye solution with stirring. The taken of the samples have been realized at several time during the reaction for 300 minutes.

The retention of the anionic dye is quick at a short time and the removal starts to get slow the equilibrium is reached after 240 minutes for the three materials.

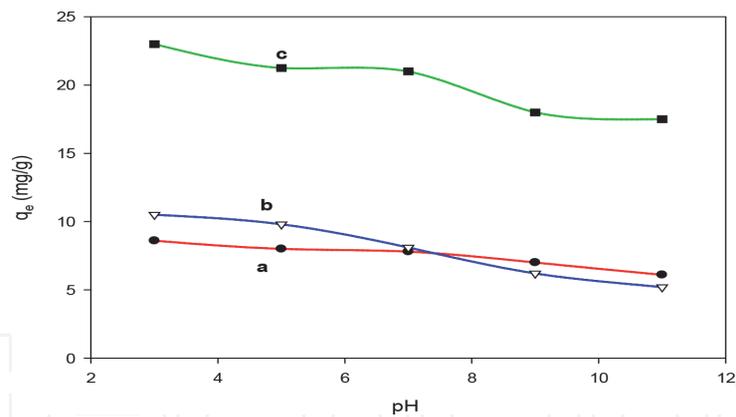


Figure 6. Effect of initial pH on the removal of AR88 dye by (a) natural phosphate, (b) phosphogypsum, and (c) phosphate waste rock.

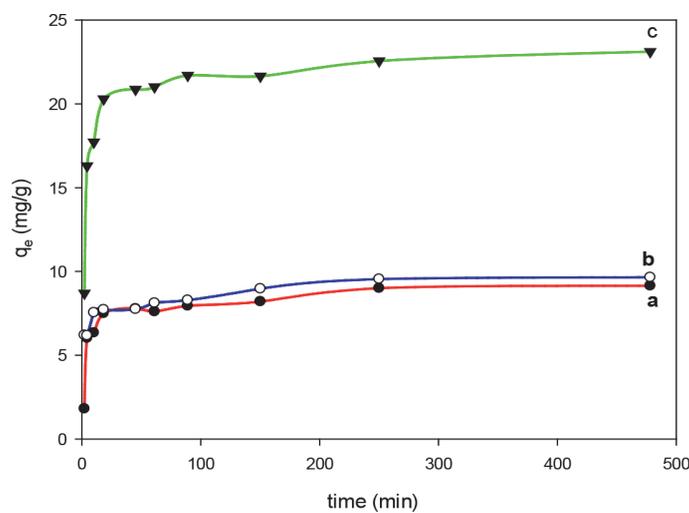


Figure 7. Removal kinetics of AR88 on (a) natural phosphate, (b) phosphogypsum and (c) phosphate waste rock.

These results can be explained by the important number of existing sites for the acid dye during the removal process.

Near to equilibrium, the number of sites is decreasing. What's more, the repulsive forces between the textile dye on the adsorbents and those in the solution are responsible of the to slow down of the speed adsorption [54, 55].

3.2.3.1 Pseudo-first-order kinetic model

This model describes the rate of change that occurs for the dye uptake [56, 57]. It is defined by Eq. (3):

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2,3} \quad (3)$$

where q_e and q_t are the removal capacities at equilibrium and time “t”, respectively. k_1 is the first-order rate constant. The linear plot of $\log (q_e - q_t)$ vs. time “t” shows the applicability of this model for the retention of the acid dye. The parameter k_1 is illustrated in **Table 3**. This values of the three compounds are varied between 0.010 to 0.014 min^{-1} . The regression correlation coefficients R^2 are near to 0.900. While the experimental values of q_e do not match the values predicted by this model.

Samples	Pseudo first order			Pseudo second order				
	K ₁ (min ⁻¹)	q _m (mg.g ⁻¹)		R ²	K ₂ (min ⁻¹ gmg ⁻¹)	q _m (mg.g ⁻¹)		R ²
		Calculated	Experimental			Calculated	Experimental	
NP	0.0107	3.343	8.75	0.903	0.006	8.849	8.75	0.998
PG	0.0109	3.536	9.26	0.904	0.080	9.216	9.26	0.997
PWR	0.0144	6.855	21.875	0.900	0.005	1.796	21.875	0.996

Table 3. Constant rates of pseudo first order and pseudo second order for the removal of acid red 88 onto various samples.

3.2.3.2 Pseudo-second-order kinetic model

The pseudo-second-order kinetic model is illustrated in Eq. (4):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

with q_e and q_t are the quantity of acid dye adsorbed at equilibrium and measured at time t (mg g⁻¹), respectively. k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant. The various parameters of the pseudo-second-order model are given in **Table 3**. The k_2 values are varied between 0.005 and 0.008 g mg⁻¹ min⁻¹. The calculated regression coefficient parameter (R^2) is near to 0.9964.

The values of the regression coefficients (R^2) near to 1 and the coincidence between the experimental results of q_e and the calculated values ones (**Table 3**) show that the retention process of anionic dye by the three compounds is characterized by the pseudo-second-order model and no than the pseudo-first-order kinetic type. Analog results have been observed for the adsorption of several textiles dyes [58–60].

3.2.4 Effect of initial concentrations

The impact of varying concentration of AR 88 on the adsorbed quantities onto PN, PG and PWR crudes of acid and basic dyes are showed in **Figure 8**. The adsorbed quantity of the acid textile dye hits a value near to 105 mg.g⁻¹ when the C_i of AR 88 is 200 mg L⁻¹ for the byproduct of a phosphate company's washing plant

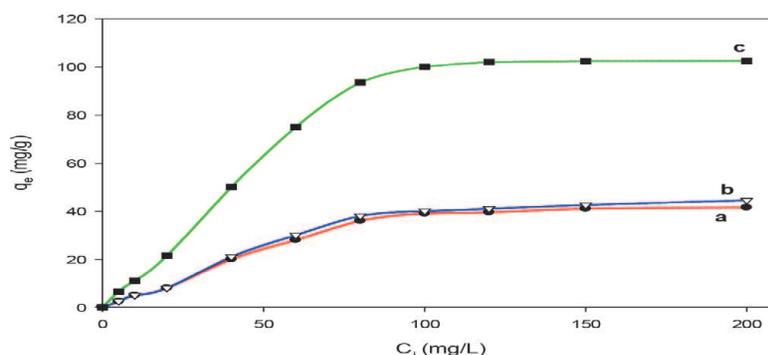


Figure 8. Variation of removed amount of AR88 (q_e (mg/g)) as in function of initial concentration (C_i (mg/L)) using (a) natural phosphate, (b) phosphogypsum, and (c) phosphate waste rock at room temperature.

sample. For the Natural Phosphate and phosphogypsum samples, the retained dye diminished to 40 and 43 mg g⁻¹, respectively.

At lower concentrations, the amount of the sites on the surface of the adsorbents compared to the number of dye molecules in the solution is important, and consequently, the acid dyes products interact with the samples. At higher concentrations, the AR 88 dye will be unavailable to contact surface sites filled [61].

3.2.5 Isotherms models

The analysis of the isotherm is an important step to optimize the design of the removal process [62]. Langmuir and Freundlich are often used to describe equilibrium isotherms. The Langmuir model is commonly applied to a complete homogeneous surface when the interaction between adsorbed molecules is negligible [63].

3.2.5.1 Langmuir isotherm model

The linear equation of the Langmuir model is expressed in Eq. (5):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} \cdot K_L} + \frac{C_e}{q_{\max}} \quad (5)$$

where q_e and C_e are the removed amount of dye (mg/g) and the concentration (mg L⁻¹) in the solution at equilibrium, respectively. q_{\max} is the maximum removed amount (mg/g), and K_L (L/mg) is the Langmuir constant. The linear plot of C_e/q_e versus C_e was used to evaluate these constants.

In the case of the Langmuir model, the constants obtained for the removal of the AR 88 dye by the NP, PG, and PWR materials are presented in **Table 4**. The values of regression correlation coefficients (R²) are higher than 0.999. These values revealed that the retention of the acid dye by the three compounds from the phosphate industry is accurately described by the Langmuir model. The estimated maximum removal capacities (q_m) are 48.4, 49.0, and 123.4 mg/g for NP, PG, and PWR, respectively. Moreover, the K_L values range between 0.032 and 0.035 L/mg.

A dimensionless constant separation factor or equilibrium parameter “ R_L ”, a characteristic of a Langmuir isotherm, is defined in Eq. (6):

$$R_L = \frac{1}{1 + K_L C_i} \quad (6)$$

with C_i is the initial concentration (mg L⁻¹), and K_L is the Langmuir constant (L/mg). Parameters of R_L in the range zero and one ($0 < R_L < 1$) reveals that the

Isotherm model	Parameters	NP	PG	PWR
Langmuir	$q_{m \text{ exp}}$ (mg g ⁻¹)	48.40	49.00	123.45
	K_L (L mg ⁻¹)	0.032	0.033	0.035
	R^2	0.997	0.993	0.994
Freundlich	K_F (L mg ⁻¹)	0.729	0.671	1.459
	n	0.83	0.85	0.84
	R^2	0.978	0.976	0.978

Table 4. Langmuir and Freundlich constants, for the removal of acid red 88 onto various samples.

retention is favorable; the adsorption is linear for $R_L = 1$, unfavorable for R_L greater than 1, and irreversible when R_L is equal to 0. In our case, R_L values were determined to be between 0 and 1, indicating the favorable adsorption of the dye to all adsorbents [64].

3.2.5.2 Freundlich isotherm model

The removal of AR88 by the different materials was also fitted to the Freundlich model [65] with the linear equation in Eq. (7):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

with the adsorbed quantity (q_e , $\text{mg}\cdot\text{g}^{-1}$) is linearly joined to the concentration of the anionic dye at equilibrium (C_e), and K_F and $1/n$ are the Freundlich constants. K_F is a combined measure of both the retention capacity and affinity, and $1/n$ informs about the degree or intensity of the retention of anionic dye. The favorability of the retention is given by the magnitude of n , i.e., values of $1/n$ less than 1 ($0 < 1/n < 1$) [66].

The values of the determined Freundlich parameters are given in **Table 4**. The acid dye affinity measured by the coefficient (OF) is in the order, phosphate waste rock > natural phosphate > phosphogypsum. The values of the $1/n$ parameter are inferior to 1, revealing that the retention of acid dye is favorable in operators' conditions. The R^2 values determined by the Freundlich model are near to 0.971 inferior that those calculated by the Langmuir model revelation that the experimental data fit well to the Langmuir isotherm model.

The obtained results indicate that, during the retention of textile dye, the last product is transferred to energetically equivalent sites, with the acid dye molecules forming a monolayer on the outer surface of the used adsorbents.

3.2.6 Effect of adsorption temperature

Temperature is a crucial parameter that affects the removal process and enables the determination of thermodynamic parameters. The effect of temperature on the adsorbed amount of NP, PG and PWR were investigated. A series of experiments were performed while maintaining the concentration of AR 88 at 200 mg L^{-1} .

The removal of AR 88 decreased at equilibrium with an increase in temperature, indicating that the removal is an exothermic process [67]. The removal process in the case is an endothermic [67]. Changes in thermodynamic parameters, such as (ΔG°), (ΔH°), and (ΔS°), were calculated by the following equations [68, 69]:

$$\Delta G^\circ = \Delta H^\circ + T\Delta S^\circ \quad (8)$$

$$\Delta G^\circ_{\text{ads}} = -RT \ln K_c \quad (9)$$

$$\ln K_c = \left(\frac{\Delta S^\circ}{R} \right) - \left(\frac{\Delta H^\circ}{R} \right) \frac{1}{T} \quad (10)$$

where K_c is the distribution coefficient of AR 88 removal from aqueous solution by waste materials, "T" is the absolute temperature, and R is the gas constant.

Table 5 summarizes the estimated thermodynamic parameters. The negative values of ΔG° at various temperatures indicate the spontaneous nature of the removal process. The negative values of H° confirm that the removal of dye using the various samples is an exothermic process [68].

Samples	H° (kJ mol ⁻¹)	S° (kJ mol ⁻¹)	G° (kJ mol ⁻¹)	R ²
NP	-13.082	-37.805	13.08	0.985
PG	-15.335	-48.223	-15.33	0.992
PWR	-83.133	-16.255	-83.13	0.997

Table 5.
Thermodynamic parameters for the retention of anionic dye on various compounds.

The negative ΔS° accompanying the removal of AR 88 indicates a less disordered system accompanied by a reduction in the randomness of the dye molecules at the solid-liquid interface.

The negative values of ΔG° indicated the spontaneous nature of the removal process. Similar data were reported for different used adsorbents. The ΔG° values are $-15.33 \text{ kJ mol}^{-1}$ (for PG) and $-13.08 \text{ kJ mol}^{-1}$ (for NP) in the case of the removal of AR 88 dye. These values represent major physical adsorption [70]. On the other hand, the removal process with PWR for the retention of the AR 88 dye characterized by chemical adsorption, where the change in free energy (ΔG°) value is $-83.13 \text{ kJ mol}^{-1}$. This process involves strong forces of attraction [71, 72]. The rise of the change in free energy (ΔG°) values with temperature could be attributed to a diminish in the molecular order during the removal process.

4. Regeneration data

The recycle of adsorbents is a very important and crucial factor to propose an efficient adsorbent. A good adsorbent supposes to have higher removal capacity as well as regeneration efficiency that will reduce the total cost of the wasted adsorbent [73].

Different methods of regeneration were reported in the literature, including two ways, washing of the used samples with different solutions such ethanol, acidic or basic ones to remove the adsorbed dyes as they are [73, 74], or to destroy the adsorbed dyes by thermal treatment at certain temperatures [75], this process will add additional costs to the process due the extra energy consumption. Another method was proposed by other researchers to destroy the adsorbed dyes on the surface of the solids via sulphate radical oxidation. This method was reported to be friendly to the environment since the solution could be used for many regeneration tests [26].

After the step of the retention of the anionic dye, the regeneration and consumption of the waste adsorbents indicates the valuable and the feasibility of their application. The **Figure 9**, show the adsorption efficiency is decreased, between 90% and 85%, regarding the byproduct of a phosphate washing sample for at least four try. Also, the other two samples: Natural Phosphate and phosphogypsum, reveals their retention percentages diminish up to 70% after three regeneration cycles. Overall, the retention efficiency is maintained at 60% for the seventh regeneration cycle.

The study of the adsorption isotherms can be used to study the removal systems. The design objective was to minimize the solid adsorbent for a specific volume of initial concentration.

The study of the adsorption isotherms can be used to study the removal systems. The aim of this study was to reduce the solid adsorbent for a specific volume of initial concentration.

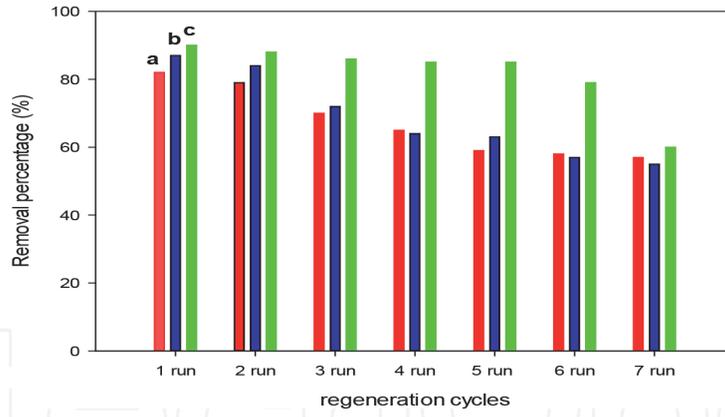


Figure 9. The percentage removal of AR88 after different regeneration cycles, (a) natural phosphate, (b) phosphogypsum, and (c) phosphate waste rock.

Consider an effluent containing V (L) of the solution in contact with the colorant and let the dye concentration got reduced from C_0 to C_1 mg dye L^{-1} solution. For a quantity of adsorbent m (g), the solute loading changed from q_0 to q_1 (mg dye per g adsorbent). When fresh adsorbent is used, $q_0 = 0$, the mass balance for the methylene blue (MB) dye in the single-stage operation under equilibrium is presented in Eq. (11).

$$V(C_0 - C_e) = m(q_0 - q_e) = mq_e \quad (11)$$

In the present case, the removal of AR 88 corresponded well with the Langmuir isotherm. Consequently, the Langmuir equation can be substituted in the Eq. (5), and the rearranged form is given in Eq. (12).

$$\frac{m}{V} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{\frac{q_m K_L C_e}{1 + K_L C_e}} \quad (12)$$

Figure 10 represent the plots derived from Eq. (12) to predict the amount of phosphogypsum and PWR required (g) to treat different effluent volumes of the

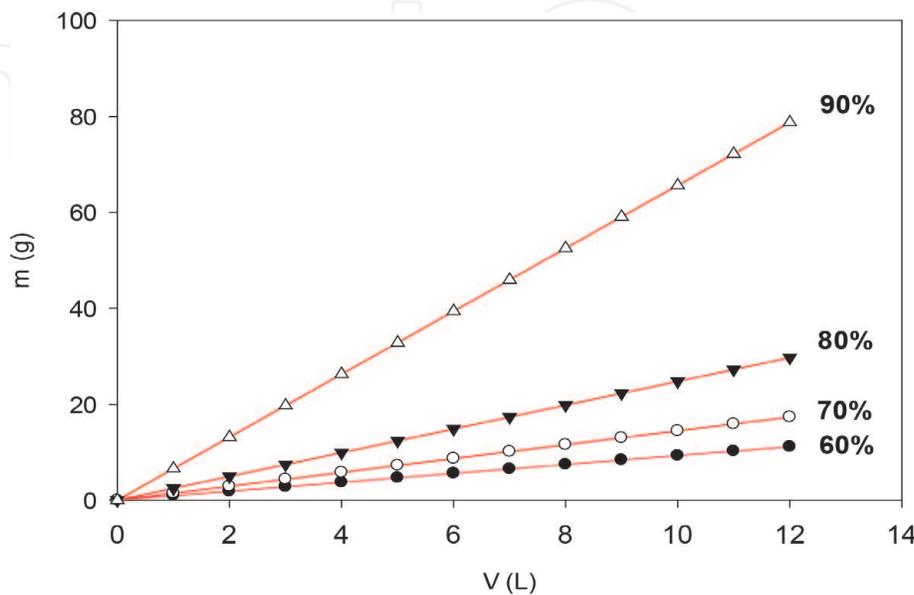


Figure 10. Predicted mass (m) of PG waste to treat different volumes (V) of AR-88 solutions, at initial concentration of 100 mg/L.

initial concentration of 100 mg L^{-1} for 60%, 70%, 80%, and 90% MB removal at different MB solution volumes from 1 to 12 L in 1 L increment. For a single design, the amount of phosphate wastes can be predicted in the range of 11 to 78.78 g for phosphogypsum and 4 to 24.97 g for phosphate waste rock materials. That is to say that the amount required for 90% removal of MB solution of the initial concentration of 100 mg L^{-1} , was about 78.78 g of PG, and 24.97 g of PWR solids, respectively. The lower mass's values for phosphate waste rock solid were associated to their higher efficiency to remove acid dyes compared to phosphogypsum waste. These data indicated that these materials could be useful as removal agents for anionic dye.

5. Conclusions

The use of byproducts from the phosphate industry could create opportunities for the treatment of water contaminated by textile dyes. This study shows that natural phosphate, phosphogypsum, and phosphate waste rock are indeed appropriate for anionic dye removal. However, phosphate waste rock (123.4 mg.g^{-1}) has a removal capacity that is higher than that of the natural phosphate (48.4 mg.g^{-1}) and phosphogypsum (49.0 mg.g^{-1}) materials.

The removal is dependent on the pH of the dye solution, with higher uptake of the dye at a lower pH in the case of the acid dye. The quantity retained increases when the pH increases for the basic dye.

The removal rate of the acid dye fits the pseudo-second-order model for all three materials. The Langmuir isotherm model more appropriately explains the experimental data while, it suggests the formation of a dye monolayer on the surface of the waste products. The Freundlich model isotherm explained appropriately the experimental data, and it suggests the heterogeneity of the surface and presumes that the adsorption takes place at sites with different adsorption energies.

In the case of acid dye, the thermodynamic parameters revealed that the removal process is spontaneous, exothermic, and occurred via chemisorption with the phosphate waste rock. However, physisorption is the proposed mechanism of removal with natural phosphate and phosphogypsum.

For the anionic dye, the regeneration of waste byproducts reveals that close to 80% of the retention dye was adsorbed after four cycles for the phosphate waste rock compound, and it was diminished to 60% after its consumption for seven cycles for all the adsorbents. A trials design was proposed, these experiences are based on the Langmuir model and the high adsorbed quantity. The sought mass of phosphate reuses to achieve a constant percentage of cationic Methylene Blue dye retention, could be readily necessary. The quantity values is linked to the phosphate reuse because their difference in their retention efficiency. Nevertheless, these reported data suggested that wastewater treatment is a potential application for the waste products of phosphate mining.

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Author details

Khaled Boughzala^{1,2*} and Mustapha Hidouri³

1 Unité de Recherche Analyses et Procédés Appliqués à l'environnement, Institut Supérieur des Sciences Appliquées et Technologie de Mahdia, Mahdia, Tunisia

2 Unit Electrochemistry, Materials and Environment, University of Kairouan, Kairouan, Tunisia

3 High Institute of Applied Sciences and Technology, Gabes, Tunisia

*Address all correspondence to: khaledboughzala@gmail.com

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