CI&CEQ
Chemical Industry & Chemical Engineering Quarterly

Available online at
Association of the Chemical Engineers of Serbia *AChE*
www.ache.org.rs/CICEQ

Chem. Ind. Chem. Eng. Q. 30 (1) 35–46 (2024) CI&CEQ

CEMRE AVŞAR[1,2]
SUNA ERTUNÇ[2]

[1]Toros AGRI Industry and Trade Co. Inc. R&D Center, Mersin / Turkey

[2]Ankara University, Department of Chemical Engineering, Ankara/ Turkey

SCIENTIFIC PAPER

UDC 666.13:66:004

FLUORIDE REMOVAL FROM PHOSPHOGYPSUM: A STUDY ON A PRE-INDUSTRIAL SCALE AND ITS MATHEMATICAL ANALYSIS

Article Highlights

- A cost-effective route for fluoride removal from phopshogypsum on pre-industrial scale is proposed
- Statistical analysis and mathematical modeling were applied to the purification process
- Optimum conditions for high-performance and cost-effective industrial treatment determination

Abstract

This study discusses fluoride removal efficiency from phosphogypsum (PG) on a lab-scale experiment matrix designed by the Box-Behnken method. Temperature, solid/liquid ratio, and time were supposed to influence fluoride removal efficiency from PG by various salt solution media. Experiment matrices were designed according to salt solution types: seawater, 5% NaCl, and 10% NaCl solutions. The factor-response analysis showed a direct proportionality between fluoride removal efficiency and temperature. The optimum fluoride removal conditions based on the experimental data obtained by the multi-variable design matrix were determined by the Design Expert v.12 software. The optimum temperature, time, and solid/liquid ratio were 80 °C, 3 h, and 0,174 for seawater. The software predicted a 73,31% fluoride removal efficiency at the optimum conditions, whereas the experimental value was 74,99%. Since the actual vs. predicted data show high consistency, results might also be useful when industrial-scale fluoride removal to a predetermined level is required prior to a particular use of PG. PG has a high potential as an alternative raw material, and fluoride removal might be important in recycling applications. This study provides a novel pre-industrial scale fluoride removal inventory, especially for the fertilizer and cement industry.

Keywords: phosphogypsum, fluoride removal, Box-Behnken design, response surface methodology.

Phosphogypsum (PG), a by-product of the manufacturing of phosphoric acid using the wet process route, can be chemically defined as impure gypsum in dihydrate form (>95 wt% $CaSO_4{\cdot}2H_2O$). Due to the reaction stoichiometry, PG (by-product) is generated five folds than H_3PO_4 (desired product) by mass. PG is discharged from the process followed by the reaction and stored as piles along coastal areas. In most cases, PG piles are left untreated, which poses a risk of impurity leakage into the groundwater during long-term storage periods. It is challenging to categorize PG using a single formulation since numerous process variables influence the chemical structure of the substance. Fluorides, heavy metals, and radionuclides originated from phosphate rocks used as the raw material in the wet process, and P_2O_5, the process residue, can all be categorized as impurities in the PG structure. One of the key elements influencing the retention of the utilization rate is the type and quantity of impurities in the chemical composition of PG. However, since PG has a chemical composition

---

Correspondence: C. Avşar, Toros AGRI Industry and Trade Co. Inc. R&D Center, 33020, Mersin / Turkey.
E-mail: cemre.avsar@toros.com.tr
Paper received: 3 February, 2023
Paper revised: 3 May, 2023
Paper accepted: 4 June, 2023

https://doi.org/10.2298/CICEQ230203009A

containing more than 95% $CaSO_4 \cdot 2H_2O$, it can efficiently serve as an alternative to gypsum. The fluoride content in PG must meet the requirement of 0.18 wt% for probable future utilization in the cement industry, even though recycling applications of PG are typically conducted in this sector. Since the average amount of fluoride in PG samples from different parts of the world is 0.9 weight percent, investigations on fluoride removal are crucial to ensure the recycling of PG [1,2]. This study provides potential environmental and industrial prospects. Concentration prediction of a specific impurity and establishing a correlation between a predetermined factor and the impurity concentration might be necessary to take action in the case of potential environmental risks. In this manner, this study provides a practical approach to the relationship between fluoride concentration and temperature. It helps to predict the possible fluoride leakages from PG piles to groundwater according to temperature variations during storage periods. From a circular economy perspective, using industrial wastes by enabling continuous circularity in production chains is important to provide sustainable resources. However, the chemical content of industrial wastes might not be appropriate for direct recycling, and purification studies might be required. PG is a potential and promising input for the cement industry, and initial fluoride concentration affects its performance in cement industry-related applications. The practical relationship between temperature and fluoride removal from PG provided by this study is a strategical highlight since the output can be industrially applicable in the case where the fluoride concentration of PG is higher than the limit levels, and fluoride removal is of importance for the utilization of PG sample in the cement industry.

Different methodologies, such as pre-treatment with different salt solutions, have been developed on the industrial recovery of PG material, whose use as a raw material is very limited due to the impurities such as heavy metals, and it has been presented to the manufacturer as an alternative to provide waste management control. Due to the optimum conditions provided by this study, the ease of application of the proposed method of pre-treatment with seawater benefits the industry by providing cost advantages to fertilizer producers.

PG recycling

The conventional economy's linear flow-based strategy makes it possible to use finite resources continuously. Additionally, the ecology is negatively affected by ineffective waste management. However, the circular economy's design principles are based on the cyclic flow of raw materials utilized in industrial applications along with efficient energy utilization. The circular flow of raw materials for effective and sustainable consumption is enabled by sustainable development goals, which internalize the circular economy strategy. Utilizing industrial wastes as process input and incorporating renewable resources into current manufacturing processes would fit under the sustainable development goals concept [3,4]. Through recycling procedures, waste management solutions in a circular economy encourage the cyclic flow of materials. Therefore, there should be a greater variety of waste management applications [5]. The phosphate fertilizer industry is one of the industries facing the challenge of generating vast waste products from wet-process phosphoric acid production.

The main input in the phosphate-based fertilizer production process is phosphoric acid. When considering the economic viability of producing phosphoric acid on an industrial scale, the wet process, which involves dissolving natural phosphate rock in sulfuric acid, is the most desirable method [6,7]. The process outputs are about 26%–32% P_2O_5-involving phosphoric acid and impure gypsum precipitate. This precipitate is known as PG, and its chemical composition includes radionuclides derived from phosphate rocks, fluorine, heavy metals, and P_2O_5 as the by-product of wet processing. According to recent figures, 300 Mtons of PG are produced annually [8–10].

The European Union (EU) categorizes PG as hazardous waste, although it can be used as a high-quality gypsum alternative. But PG may be categorized as non-hazardous waste if it satisfies the requirements of the hazard property codes for a particular application area [4,11,12]. The usage rate is hampered by the PG's classification as hazardous waste. Huge amounts of PG remain untreated due to its 15% recycling rate [13]. Basic issues with the management PG include the land cost of the piles and remediation expenditures related to reducing environmental degradation [14–16]. Recent research on using PG for various industrial applications highlights the need to create an environmentally friendly recycling system that permits the widespread use of PG.

PG and fluoride removal

The primary component impacting the chemical structure of PG is phosphate rock, utilized as the input of the wet process. Besides, other operational process variables, like process effectiveness, post-production disposal strategies, and the PG stack's physical state, also impact the PG structure [17]. PG is challenging to specify in a single formulation due to its variable chemical structure, although the amount of impurities is considered within a predetermined range.

Fluoride is one of the impurities in PG composition, and the approximate amount of fluoride is 0.9% wt among PG samples found worldwide. Fluoride is an important trace element for living bodies; however, excess fluoride input might affect various organs and systems. Developments in agricultural and industrial applications have triggered the irrepressible fluoride release to the environment, and today fluoride pollution in any form of environment, aquatic or human life, has become a serious problem [18]. Fluoride release from various minerals, such as fluorite, tourmaline, biotite, quartz, kyanite, etc., is commonly encountered. Among these minerals, gypsum is another fluoride source, and release mechanisms are noted to actualize in a wide range of pH values [19]. The average fluoride content in worldwide PG samples is mostly below 0.9 wt%, except for the Tunisian and Algerian samples. These samples have higher fluoride concentrations than the other PG samples.

In contrast, the rest samples have similar fluoride amounts, being approximately below 0.9 wt%, being independent of the year and location of the sample. Fluoride concentrations of PG samples might be relevant to the age of the PG piles. Fluorite and fluorapatite are the dominant mineral phases affecting the fluoride concentration in PG. During the long-term storage period, approximately 0.1 wt% fluoride in PG is released into the gaseous phase, whereas the accumulation of precipitated fluoride complexes in soils as in the form of CaF_2 and $Ca_5(PO_4)_3F$ might also occur [20,21]. Natural fluoride minerals like fluorspar (CaF_2), fluorapatite ($Ca_3(PO_4)_2Ca(FCl_2)$), cryolite (Na_3AlF_6), and sellaite (MgF_2) have very low solubility in water. Still, because PG stacks are frequently deposited along marine coastlines like many other industrial by-products, fluoride leakage may occur over an extended time under favorable conditions. During long-term storage periods, the leakage of water-soluble pollutants negatively influence the residential area by changing the chemical composition of groundwater and having a hydrodynamic impact on the environment [20,21]. Hence, industrial effluents are more dominant as fluoride sources in aqueous media. The fluoride concentration in the effluent streams should be periodically controlled within the regulatory orientations [22,23].

Although the effect mechanism of fluoride cannot be systematically described, kinetic, thermodynamic, and molecular modeling simulations can be applied for fluoride leachability [24]. Fluoride naturally occurs in groundwater; however, many the industries, such as metallurgy, iron-steel, copper, battery, and cement, discharge effluents containing fluoride about 250 ppm–1500 ppm and might reach up to 10.000 ppm in extreme cases [25,26]. PG is a different case since it is not an industrial effluent but a solid waste stacked and formed sediments in long-term storage periods. PG stacks are generally located near coastal areas, and fluoride leakage into groundwater might occur during storage. This phenomenon reduces the initial fluoride content in PG, transferring fluoride into groundwater; thus, this naturally occurring process can also be termed as fluoride removal. PG contains some impurities depending on the phosphate rock used in the wet process and process residues in its chemical structure. The removal of these impurities in the experimental studies indicates that PG does not contain more than any industrial pollutants depending on its solubility ratio. It has been determined that no contamination or toxicity has been found in the samples taken from the environment where PG is discharged. However, after the production of H_3PO_4, an important development has been achieved regarding heavy metal removal by chemical precipitation method and minimizing environmental problems.

Chemical, physical, and thermal processes are used to remove impurities from PG. Combinations of these techniques are also used in some situations. For purification, PG is typically treated with ammonium hydroxide, citric acid, sulfuric acid, or dissolved lime; flotation or calcination is also used to remove impurities [27–29,12]. The crystalline gypsum structure is degraded during chemical impurity removal processes that involve sulfate ion replacement [30]. In this way, impurity removal from salt solution can be successful without causing crystalline structure degradation. Results for the use of seawater could help forecast PG-stack-based leaks over long-term storage periods [31,32].

Box Behnken design of the response surface methodology

Traditional optimization studies rely on experiment conduction as one factor at a time (OFAT). This strategy relies on the variation of one variable or factor at a time, keeping other variables constant. This approach is generally impractical when conducting all necessary experiments with each possible factorial combination. The time-consuming disadvantage of the conventional method can be turned off by the optimization of all the variables simultaneously by statistical experimental design. Response surface methodology, which analyzes an empirical model using a combination of statistical and mathematical techniques, is particularly appropriate for studies involving particular experiment designs because it allows for the minimization of the number of runs that an experiment set must undergo for a given set of factors and factor levels [33,34].

RSM is a highly effective approach when determining the optimum operational conditions in a specific experimental setup or a region within the limits of specified optimum experimental conditions [35]. One of the design matrices in RSM is the Box-Behnken design (BBD), which includes multivariable, 2nd order, rotatable, or nearly rotatable designs. Application of BBD can be conducted in two different forms, one of which is a central point and the middle points of the edges, and the other is a 2^2 factorial design and a central point. When an evaluation is required under challenging experimental settings and to ascertain the reaction of the function on its maxima or minima, this form of experimental design can be beneficial [36].

Tetteh and Rathilal studied the biogas and decontamination removal efficiency of bio photocatalytic degradation of municipality wastewater by using RSM based on a modified BBD experiment to optimize and maximize the desirability of the bio photocatalytic system. The modified RSM-BBD model was studied to determine the optimum catalyst load, hydraulic retention time, and temperature. Experimental verification results showed a high agreement with the predicted results in the RSM-BBD model at a high regression ($R^2 > 0.98$) and within the range of 95% confidence level [37]. Another modeling and optimization study using RSM on industrial wastewater treatment with 17 experimental runs was conducted by introducing coagulant dosage, settling time, and mixing rate as the variables in the design matrix. The predictability of the RSM model was validated using an artificial neural network (ANN). The results were in agreement with the RSM model, where the coefficient of determination (R^2) was 0.994 for the ANN model and 0.97 for the RSM model, within the range of 95% confidence level ($p<0.05$) [38]. Apart from these model prediction and optimization studies using RSM for industrial wastewater treatment applications, some studies regarding fluoride removal are also available in the literature.

Mourabet *et al.* employed a BBD by introducing starting concentration, temperature, adsorbent dosage, and pH as the input parameters in an aqueous solution [35]. The RSM was used to optimize fluoride removal with apatitic tricalcium phosphate. Results indicated that a second-order polynomial model, with an R^2 value of 0.966, provided a good fit for the regression analysis and experimental results [35]. El-Din Mohamed *et al.* conducted a study to compare the outcomes of OFAT and BBD, and a fluoride biosorption optimization study using *Padina sp.* algae as the biosorbent was carried out [39]. The maximum amount of fluoride removed, according to OFAT data, was 85.95%; however, according to the BBD results, the maximum amount of fluoride removed was 94.57%. ANOVA analysis was used to determine the statistical significance of the constructed model, and RSM was found to be more useful for efficient optimization [39].

This study gives a novel approach and a brief demonstration of fluoride removal efficiency upon salt solution treatment of PG according to a multi-variable BBD with time, solid/liquid (w/v) ratio and temperature as the parameters in various salt solution media. Seawater and 5% NaCl and 10% NaCl solutions were studied to investigate the fluoride removal efficiency from PG, and lab-scale experiment results were simulated in Design Expert v.12 software. Since PG piles are located near coastal regions and seawater is investigated as a salt solution media, this study might be useful to predict the quantity of real-time fluoride leakage to the sea ecosystem. Another study highlight is the computational approach to fluoride removal from PG, enabling a straightforward prediction when fluoride impurity is important. PG-related industries might favor the outputs of this study for particular reasons. For example, the fertilizer industry might benefit from periodic regulatory controls of groundwater fluoride concentrations near PG piles. The outputs of this study might be effective in setting up a correlation between fluoride leakage and seasonal temperature variations, and precautions can be taken before regulatory controls do not cause abnormal fluoride concentrations in the groundwater near PG piles. The cement industry also utilizes PG recycling strategies; however, the changeable chemical of PG might not always be appropriate in terms of fluoride concentration, and there would be some cases for prior purification. The study outputs might benefit the cement industry for a practical fluoride content analysis in the PG before its process applications.

MATERIAL AND METHODS

Experimental

PG samples used in the study were provided by Toros Agri Industry anf Trade Co. Inc. (Mersin/Turkey). The initial PG sample has a free water content of 13%, a slightly acidic pH of 4.8 to 6, and conductivity of 2230 µmhos/cm to 2320 µmhos/cm. Mineralogy characterization showed a 99.4% dihydrate gypsum with trace amounts of quartz, anhydrite, and bassanite. PG samples showed a variable morphology from stubby, lath-shaped crystals to irregularly-shaped crystals and brown to light brown appearance in color. Particle size distribution showed 97% silt-size particles and 3% fine sand-size particles, with a mean particle diameter of 25 µm to 32 µm.

Besides seawater (sampled near PG stack, a region near Mersin Port, Mediterranean Sea), 5% and 10% (wt%) NaCl solutions were used to remove fluoride from PG and to determine the appropriate salt solution.

Evaporation yielded a 5% (wt%) salt concentration for seawater, and NaCl solutions with 5% and 10% (wt%) were prepared compared to seawater in terms of concentration and salt type. The salt solutions of 5% and 10% NaCl were determined to be a single type of salt with the same concentration and concentrated salt amount, respectively. Seawater is assumed to be a mixture of different salt types. The BBD matrix for three factors is shown in Table 1, with five replicates at the center points and both coded and real values. In accordance with the design matrix shown in Table 1, experiment runs were carried out to examine the impacts of multivariable parameters and identify the ideal conditions for the removal of fluoride from PG into aqueous salt solutions. The three independent variables were temperature (20-80 °C), time (3 h–6 h), and the solid/liquid ratio (0.1 w/v–0.2, w/v). The efficacy of fluoride removal was examined according to the interactions and quadratic effects of the various parameters. The salt solution type is regarded as a variable because the experiments shown in Table 1 were carried out with the abovementioned salt solution systems. All the experiments were carried out randomly and in triplicates to minimize the unexplained variation in responses owing to systematic errors.

Table 1. Box-Behnken design matrix for three factors, both coded and actual values.

Run #	A: Temperature (°C)	B: Time (h)	C: Solid/Liquid Ratio (w/v)
1	50 (0)	3 (-1)	0.2 (+1)
2	80 (+1)	4.5 (0)	0.1(-1)
3	50 (0)	4.5 (0)	0.15 (0)
4	20 (-1)	6 (+1)	0.15 (0)
5	50 (0)	3 (-1)	0.1 (-1)
6	50 (0)	4.5 (0)	0.15 (0)
7	20 (-1)	4.5 (0)	0.2 (+1)
8	20 (-1)	3 (-1)	0.15 (0)
9	80 (+1)	4.5 (0)	0.2 (+1)
10	50 (0)	4.5 (0)	0.15 (0)
11	50 (0)	6 (+1)	0.2 (+1)
12	80 (+1)	3 (-1)	0.15 (0)
13	50 (0)	4.5 (0)	0.15 (0)
14	50 (0)	4.5 (0)	0.15 (0)
15	20 (-1)	4.5 (0)	0.1 (-1)
16	80 (+1)	6 (+1)	0.15 (0)
17	50 (0)	6 (+1)	0.1 (-1)

10 g of sieved PG samples with particle sizes of less than 125 µm were weighed, and the experiment runs listed in Table 1 were carried out in solutions of 5% and 10% NaCl and seawater. After each experiment, a filter was applied to the PG/salt solution system. UV-Spectrophotometry was used to measure the fluoride concentration in experiment supernatants (HACH Lange DR 3900 UV Spectrophotometer).

The degree of fluoride removal efficiency was calculated according to Eq. (1), where $F_{supernatant}$ is the fluoride concentration of the supernatant of PG/salt solution samples stirred after specified time according to BBD matrix, and $F_{salt\ solution,\ initial}$ and $F_{initial,PG}$ are the initial fluoride content of the salt solution and PG sample, respectively. $F_{salt\ solution,\ initial}$ and $F_{initial,PG}$ values are given in Table 2.

$$\mathit{Fluoride\ removal\ efficiency}\,(\%) = \frac{F_{\mathrm{supernatant}} - F_{\mathrm{salt\ solution,\ initial}}}{F_{initial,PG}} \cdot 100 \qquad (1)$$

The fluoride removal performance of seawater and 5% and 10% NaCl solutions were compared. The most suitable among them were selected, and the factor levels were optimized for maximum fluoride removal efficiency defined with Eq. (1). The resulting data were fitted to a second-order polynomial model including main, interaction, and quadratic effects of the variables (factors) on the response variable. The statistical significance of the variables was determined using Analysis of Variance (ANOVA) with a confidence level of 95%. Moreover, the developed model's adequacy was estimated by evaluating the lack of fit test and determination coefficient (R^2) obtained from ANOVA.

Predicted values were plotted against the actual responses for each salt solution treatment to show the explanation performance of the model in the experimental data.

A detailed schematic illustration of the sampling, model design, experimental study, and data analysis throughout the study is given in Figure 1.

RESULTS AND DISCUSSION

The initial fluoride concentrations of each salt solution are listed in Table 2, which serves as a starting point for the computation of the fluoride removal efficiency shown in Eq.(1). Removal efficiency values for each of the experiment sets were calculated from the fluoride concentrations of all the supernatant samples measurements obtained by three replications, were given in Table 3.

Fluoride removal was estimated in each salt solution system, and the removal rates in each system

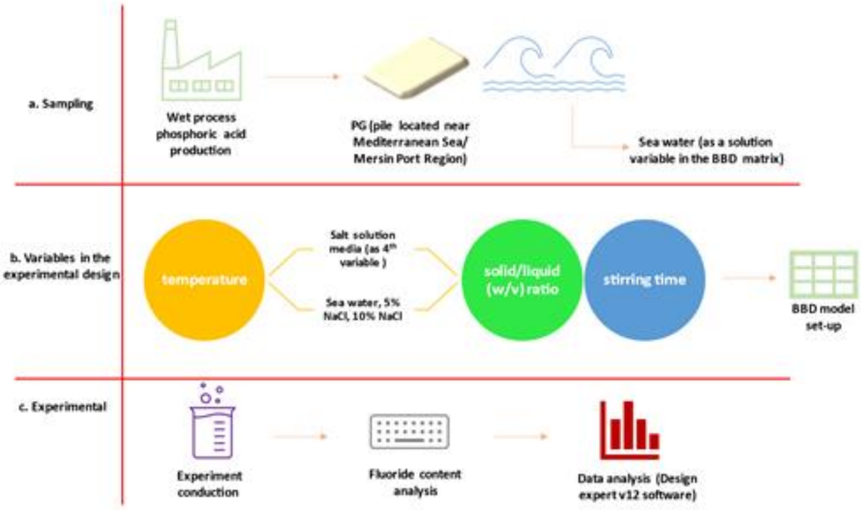

Figure 1. Schematic illustration of the study.

Eq.(1) revealed a continuous variation strongly influenced by temperature. Thus, Table 3 shows the reorganized version of the BBD matrix according to temperature to observe the fluoride removal efficiency upon the change in the temperature of the salt solution systems.

Table 2. Initial fluoride concentrations (ppm).

Sample	Fluoride (ppm)
PG	96
Seawater	7.6
5% NaCl solution	3.6
10% NaCl solution	5.6

Table 3 shows that the efficiency of removing fluoride from all solutions is exactly proportional to temperature. Figure 2 displays the average fluoride removal efficiency in several solutions according to temperature.

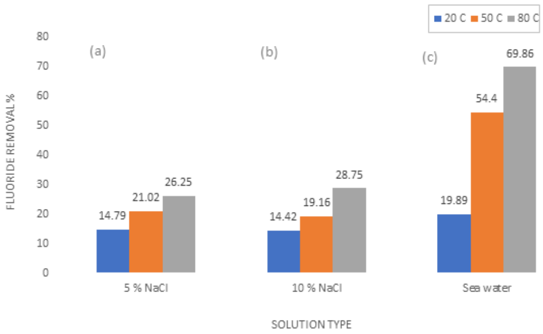

Figure 2. Fluoride removal efficiency according to temperature in (a) 5% NaCl, (b) 10% NaCl and (c) seawater.

Table 3. Box-Behnken design matrix for fluoride removal efficiencies from PG.

Run #	Temperature (°C)	Seawater	5% NaCl	10% NaCl
4	20	22.08	14.58	15.00
7	20	22.29	13.33	14.38
8	20	18.33	14.17	13.73
15	20	16.88	17.08	14.58
1	50	55.00	16.67	20.42
3	50	54.17	19.17	17.92
5	50	50.83	17.92	18.33
6	50	57.08	20.00	17.50
10	50	NA*	23.75	16.25
11	50	57.08	22.92	24.17
13	50	NA*	21.67	20.83
14	50	55.42	23.33	18.33
17	50	51.25	23.75	18.75
2	80	65.42	25.42	28.33
9	80	70.00	27.50	29.17
12	80	74.17	26.25	30.42
16	80	NA*	25.83	27.08

NA*: Not Applicable

The lowest fluoride removal efficiency was demonstrated by a 5% NaCl solution followed by a 10% NaCl solution. Seawater displayed the best fluoride removal efficiency. Similarly, average fluoride removal efficiencies at different temperatures according to salt solutions are given in Figure 3.

Seawater is a complex salt solution system,

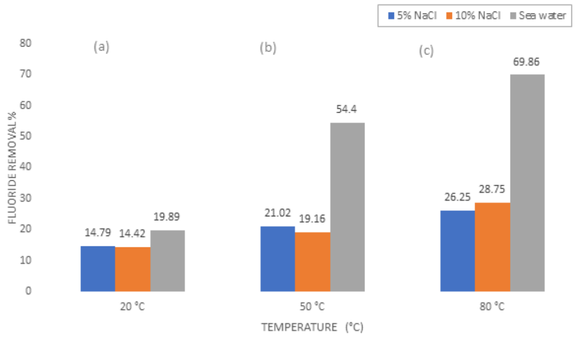

Figure 3. Fluoride removal efficiency according to salt solution type at (a) 20 °C, (b) 50 °C, and (c) 80 °C.

whereas 5% and 10% NaCl are single-salt solutions. Fluoride removal efficiency in complicated salt solution systems exhibits a greater rate, according to the removal efficiency values shown in Table 3. Temperature is a calculated multivariable included in the BBD matrix that significantly affects fluoride removal efficiency. There was a direct correlation between temperature and fluoride removal efficiency in earlier research published in the literature [40–42]. Seawater demonstrated the greatest fluoride removal efficiency regarding both solution type and temperature. The initial fluoride level of the 20-year-old PG stack was measured at 96 ppm, and the low fluoride concentration may be due to fluoride leakages during long-term storage. The first burst release was used to depict long-term fluoride release because it displays a time-decreasing pattern, and the low fluoride content of the PG stack is consistent with the data from the literature [43]. Although the sampled PG stack does not concern the environment, its purity may be problematic if the material is used as a resource.

Fluoride removal results were evaluated by Design Expert v.12 software. ANOVA analyses for each salt solution are given in Table 4 for seawater, 5% NaCl, and 10% NaCl, respectively.

Model *F*-values (199.56, 25.19, and 27.34) of each salt solution treatment result show that all models are significant. The probability that such a large *F*-value will occur due to noise is only 0.01%. *p*-values less than 0.0500 indicate that the model terms are significant. In this case, A, C, and A^2 are the important model terms for the seawater treatment. On the other hand, for the 5% and 10% NaCl purifications, the meaningful model term is only A. While the seawater treatment results are modeled with a quadratic model, 5% and 10% NaCl treatment results are modeled with the linear model, only including the main effects of the factors. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. But in this study, regression models with all the model terms, whether the model term was significant or not, were considered to predict the response variable, so the model reduction was not made. The lack of fit *F*-value of each salt solution treatment (1.58, 0.90, and 2.17) implies it is insignificant relative to the pure error. Non-significant lack of fit is good for all three models.

Regression models with coded factor values for fluoride removal efficiencies for all salt solutions were obtained as given the Eq.(2–4) below:

$$\begin{aligned}&\mathit{Fluoride\ removal\ efficiency} - \mathit{Sea\ water}\,(\%) = \\ &55.56 + 24.71A - 0.0260B + 2.50C - 2.55AB - 0.2083AC \\ &+0.4167BC - 9.94A^2 - 0.0434B^2 - 1.97C^2\end{aligned} \tag{2}$$

$$\begin{aligned}&\mathit{Fluoride\ removal\ efficiency} - 5\%\ \mathit{NaCl}\,(\%) = \\ &20.78 + 5.73A + 1.51B - 0.4688C\end{aligned} \tag{3}$$

$$\begin{aligned}&\mathit{Fluoride\ removal\ efficiency} - 10\%\ \mathit{NaCl}\,(\%) = \\ &20.31 + 7.16A + 0.2630B + 1.02C\end{aligned} \tag{4}$$

Predicted response versus actual response plots are given in Figure 4. The best model prediction was obtained for the seawater treatment with the determination coefficient value (R^2) of 0.9978. In contrast, model predictions for the 5% and 10% NaCl treatments were not good enough, with R^2-values of 0.853 and 0.863, respectively.

Since seawater was the best salt solution for fluoride removal from PG, considering both the resulted percent yields and the ANOVA analysis, 3D response surface plots were drawn to analyze the factor effects on the seawater treatment, as given in Figure 5.

Figure 5 shows no significant relationship between fluoride removal efficiency and time at lower temperatures. But, increasing temperature changes the trend, and higher fluoride efficiency can be observed in shorter periods at higher temperature ranges. The solid/liquid ratio also shows higher fluoride removal efficiency at higher temperatures. Upon the multivariable in the BBD matrix, consistent relation was observed according to temperature, and it can be said that fluoride removal efficiency is a temperature-dependent phenomenon.

The optimum temperature, time, and solid/liquid ratio were obtained to be 80 °C, 3 h, and 0.174 solid/liquid (PG/seawater, w/v) ratio, respectively, in Design Expert v.12 software, predicting a fluoride removal of 73.31% with the optimum combination of experimental parameters. Experimental verification of optimum conditions obtained by Design Expert v.12 software was also performed with a basis of 10 g PG sample, having a solid/liquid ratio of 0.174 (PG/seawater, w/v) treated at 80 °C and 3 h. Results showed 74.99% fluoride removal efficiency, which is

Table 4. ANOVA results of fluoride removal efficiencies for seawater, 5% NaCl solution, and 10% NaCl solution.

Source	Sum of squares			df			Mean square			*F*- value			*p*-value		
	NaCl (%)														
	SW[a]	5	10	SW	5	10	SW	5	10	SW	5	10	SW	5	10
Model	4967.7	282.60	419.40	9	3	3	551.98	94.20	139.80	199.56	25.19	27.34	<0.0001	<0.0001	<0.0001
A[b]	3257.38	262.59	410.59	1	1	1	3257.38	262.59	410.59	1177.64	70.22	80.29	<0.0001	<0.0001	<0.0001
B[c]	0.0036	18.25	0.5534	1	1	1	0.0036	18.25	0.5534	0.0013	4.88	0.1082	0.9729	0.0457	0.7474
C[d]	50.00	1.76	8.25	1	1	1	50.00	1.76	8.25	18.08	0.4701	1.61	0.0131	0.5050	0.2262
AB	13.03			1			13.03						0.0958		
AC	0.1736			1			0.1736			0.0628			0.8145		
BC	0.6944			1			0.6944			0.2511			0.6426		
A^2	296.37			1			296.37			107.14			0.0005		
B^2	0.0057			1			0.0057			0.0020			0.9661		
C^2	11.65			1									0.1094		
Residual	11.06	48.61	66.48	4	13	13		3.74	5.11						
Lack of fit	6.78	32.50	55.16	2	9	9		3.61	6.13		0.8966	2.17	0.3871	0.5929	0.2375
Pure error	4.28	16.11	11.32	2	4	4		4.03	2.83						
Cor total	4978.86	331.21	485.87	13	16	16									

[a] - Seawater; [b] - Temperature; [c] - Time; [d] - Solid/Liquid ratio.

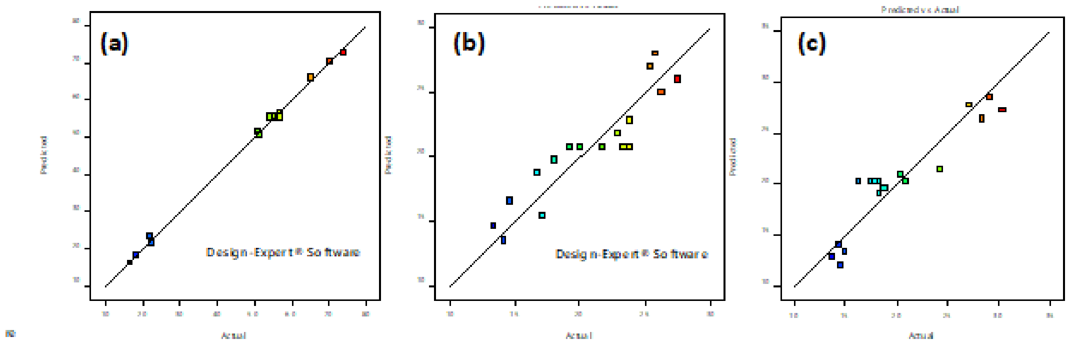

Figure 4. Predicted response versus actual response in fluoride removal efficiencies for salt solution treatments (a) seawater, (b) 5% NaCl, and (c) 10% NaCl.

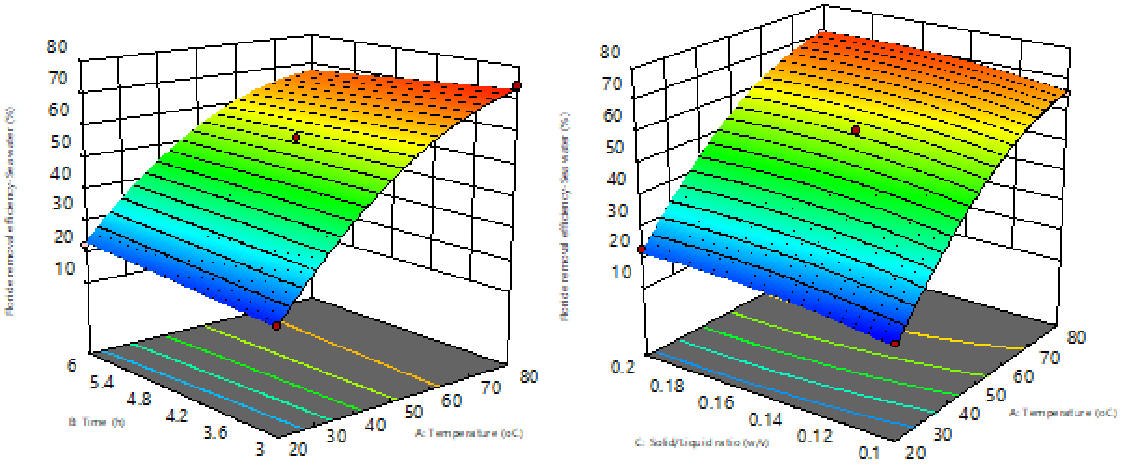

Figure 5. Response surface plots showing the interactions between process parameters for fluoride removal efficiency from PG (a) temperature and time, (b) temperature and solid/liquid ratio.

statistically within the 95% confidence range.

The use of PG material as raw material is paved with the fluoride removal method by washing with salt solutions, which is offered as an alternative to the problem of PG being formed as a by-product in large piles in phosphoric acid production and keeping them as piles without being used as raw material for any industry due to impurity content. It provides an important cost advantage for raw materials to the manufacturer.

Although the damage mechanism of fluoride in terms of leakage to groundwater or impact on the nearby marine or soil ecosystem has not been extensively defined, the study's results might be directive to predict the quantitative fluoride leakage from the PG stacks into groundwater upon seasonal temperature variations. Optimum conditions determined by the experimental data indicated that pre-treatment of PG with seawater was the most effective method for fluoride removal. The effect of seawater on fluoride removal provides a cost advantage to the industrial manufacturer, and the pollution removal with recommended seawater is ground. One of the important details of this study is that PG can be discharged without any environmental threat due to the treatment of phosphate rock or uncontrolled PG with seawater. Because a pre- or post-treatment process to be applied to the raw material or by-product with seawater can be accepted as an easy and simple method that today's fertilizer manufacturers can apply, in which phosphoric acid production is conducted.

Fluoride removal from PG is a contamination problem that has been prominent in the literature until today. However, environmental problems have been partially minimized in the proposed pollution removal methods and directed the manufacturer to alternative studies. As the focus of this article, an economical solution method that can be applied in existing phosphoric acid production facilities is presented to the producer with the pollution removal method.

CONCLUSION

The salt solution media used in this study included seawater, 5% NaCl, and 10% NaCl solutions. The results of the experimental study showed a consistent relationship based on temperature. The efficacy of fluoride elimination is, therefore, a temperature-dependent phenomenon. Optimization of the multi-response system was performed by Design Expert v.12 software, and the simulation indicated a 73,31% fluoride removal with seawater when the experiment was performed at 80 °C, 3 h, and 0,174 solid/liquid (PG/seawater, w/v) ratio, respectively. The study's results may help estimate how much fluoride will leak from PG stacks into groundwater due to temperature changes or guide fluoride removal under predetermined ideal conditions when PG purification is crucial before recycling for a particular use. The former case is in accordance with the circular economy, investigating a fluoride removal and purification study to use PG in further recycling processes. The latter case gives a brief simulation for predicting the deviations in fluoride concentrations in the groundwater related to the leakages from PG piles in different seasonal conditions.

ACKNOWLEDGMENT

This study is financially supported by The Scientific and Technological Research Council of Turkey (TÜBİTAK, Project No: 118C085) and conducted between the cooperation of Ankara University and Toros AGRI Industry and Trade Co. Inc. R&D Center within the scope of TÜBİTAK 2244 Industrial Ph.D. Fellowship Program.

NOMENCLATURE

PG	Phosphogypsum
BBD	Box-Behnken Design
RSM	Response Surface Methodology
EU	European Union
OFAT	One Factor at a Time
ANN	Artificial Neural Network
ANOVA	Analysis of Variance

REFERENCES

[1] M. Abdelhadi, N. Abdelhadi, T. El-Hasan, Earth Sci. Res. 7(2) (2018) 28–41. https://doi.org/10.3176/oil.2019.2S.12.

[2] M. Singh, M. Garg, S.S. Rehsi, Const. Build. Mater. 7(1) (1993) 3–7. https://doi.org/10.1016/0950-0618(93)90018-8.

[3] K. Chojnacka, D. Skrzypczak, K. Mikula, A. Witek-Krowiak, G. Izydorczyk, K. Kuligowski, P. Bandrow, M. Kulazynski, J. Clean. Prod. 313 (2021) 1–12. https://doi.org/10.1016/j.jclepro.2021.127902.

[4] L.F.O. Silva, M. L. S. Oliveira, T.J. Crissien, M. Santosh, J. Bolivar, L. Shao, G.L. Dotto, J. Gasparotto, M. Schindler, Chemosphere 286(1) (2022) 1–14. https://doi.org/10.1016/j.chemosphere.2021.131513.

[5] H. Salmenpera, K. Pitkänen, P. Kautto, L. Saikku, J. Clean. Prod. 280(1) (2021) 1–19. https://doi.org/10.1016/j.jclepro.2020.124339.

[6] B. Karshiev, A. Seytnazarov, U. Alimov, S. Namazov, A. Reymov, A. Rasulov, Vopr. Khim. Khim. Tekhnol. 1 (2021) 24–34. https://doi.org/10.32434/0321-4095-2021-134-1-24-34.

[7] Q. Chen, S. Sun, Y. Liu, C. Qi, H. Zhou, Q. Zhang, Int. J. Miner. Metall. 28 (2021) 1440–1452. https://doi.org/10.1007/s12613-021-2274-6.

[8] L. Feng, K. Jin, H. Wang, Coatings 11(7) (2021) 1–12. https://doi.org/10.3390/coatings11070802.

[9] L. Yang, Y. Zhang, Y. Yan, J. Clean. Prod. 127 (2016) 204–213. https://doi.org/10.1016/j.jclepro.2016.04.054.

[10] H. Wang, X. You, J. Tian, X. Cheng, J. Wang, IOP Conf. Ser.: Earth Environ. Sci. 668 (2021) 1–7. https://doi.org/10.1088/1755-1315/668/1/012076.

[11] J. Rosales, M. Gazquez, M. Cabrera, J.P. Bolivar, F. Agrela, in Waste and Bypoducts in Cement-Based Materials- Innovative Sustainable Materials for a Circular Economy, J. de Brito, C. Thomas, C. Medina, F. Agrela Ed., Woodhead Publishing, (2021) 153–189. ISBN: 9780128208953.

[12] W. Cao, W. Yi, J. Li, J. Peng, S. Yin, Const. Build. Mater. 309 (2021) 125190. https://doi.org/10.1016/j.conbuildmat.2021.125190.

[13] C.R. Canovas, R. Perez-Lopez, F. Macias, S. Chapron, J.M. Nieto, S. Pellet-Rostaing, J. Clean. Prod. 143 (2017) 497–505. https://doi.org/10.1016/j.jclepro.2016.12.083.

[14] F. Wu, S. Liu, G. Qu, B. Chen, C. Zhao, L. Liu, J. Li, Y. Ren, J. Adv. Chem. Eng. 9 (2022) 1–11. https://doi.org/10.1016/j.ceja.2021.100227.

[15] K. Ren, N. Cui, S. Zhao, K. Zheng, X. Ji, L. Feng, X. Cheng, N. Xie, Crystals 11(7) (2021) 1–20. https://doi.org/10.3390/cryst11070719.

[16] Z. Wei, Z. Deng, J. Environ. Radioact. 242 (2022) 106778. https://doi.org/10.1016/j.jenvrad.2021.106778.

[17] H. Tayibi, M. Choura, F.A. Lopez, F.J. Alguacil, A. Lopez-Delgado, J. Environ. Manage. 90(8) (2009) 2377–2386.

https://doi.org/10.1016/j.jenvman.2009.03.007.

[18] S. Wu, Y. Wang, M. Iqbal, K. Mehmood, Y. Li, Z. Tang, H. Zhang, Environ. Pollut. 304 (2022) 119241. https://doi.org/10.1016/j.envpol.2022.119241.

[19] P. Singh, A. Saxena, J. Geol. Soc. India 98 (2022) 133–138. https://doi.org/10.1007/s12594-022-1939-8.

[20] Y. Chernysh, O. Yakhnenko, V. Chubur, H. Roubik, Appl. Sci. 11 (4) (2021) 1–20. https://doi.org/10.3390/app11041575.

[21] P.M. Rutherford, M.J. Dudas, J.M. Arocena, Environ. Technol. 16(4) (1995) 343–354. https://doi.org/10.1080/09593331608616276.

[22] A. Jeyaseelan, A.A. Ghfar, M. Naushad, N. Viswanathan, J. Environ. Chem. Eng. 9(1) (2021) 1–12. https://doi.org/10.1016/j.jece.2021.105384.

[23] L. Lahlmunsiama, N. Ngainunsiami, D. Kim, D. Tiwari, Chem. Eng. Process. 165 (2021) 1–14. https://doi.org/10.1016/j.cep.2021.108428.

[24] S. Ghosh, A. Malloum, C.A. Igwegbe, J.O. Ighalo, S. Ahmadi, M.H. Dehghani, A. Othmani, Ö. Gökkuş, N.M. Mubarak, J. Mol. Liq. 346 (2022) 118257. https://doi.org/10.1016/j.molliq.2021.118257.

[25] C.F.Z. Lacson, M. Lu, Y. Huang, J. Clean. Prod. 280(1) (2021) 1–20. https://doi.org/10.1016/j.jclepro.2020.124236.

[26] K. Wan, L. Huang, J. Yan, B. Ma, X. Huang, Z. Luo, H. Zhang, T. Xiao, Sci. Total Environ. 773 (2021) 1–20. https://doi.org/10.1016/j.scitotenv.2021.145535.

[27] R. Moalla, M. Gargouri, F. Khmiri, L. Kamoun, M. Zairi, Environ. Eng. Res. 23(1) (2018) 36–45. https://doi.org/10.4491/eer.2017.055.

[28] X. Chen, J. Gao, Y., Zhao, Constr. Build. Mater. 229 (2019) 1–9. https://doi.org/10.1016/j.conbuildmat.2019.116864.

[29] M. Du, J. Wang, F. Dong, Z. Wang, F. Yang, H. Tan, K. Fu, W. Wang, Research Square, preprint 1(1) (2021) 1–19. https://doi.org/10.21203/rs.3.rs-888156/v1.

[30] J.S.A. Neto, J.D. Bersch, T.S.M. Silva, E.D. Rodriguez, S. Suziki, A.P. Kirchheim, Constr. Build. Mater. 299 (2021) 1–11. https://doi.org/10.1016/j.conbuildmat.2021.123935.

[31] B. Guan, L. Yang, H. Fu, B. Kong, T. Li, L. Yang. Chem. Eng. J. 174 (1) (2011) 296–303. https://doi.org/10.1016/j.cej.2011.09.033.

[32] Q. Guan, Y. Sui, F. Zhang, W. Yu, Y. Bo, P. Wang, W. Peng, J. Jin, Physicochem. Probl. Miner. Process. 57(1) (2021) 168–181. https://doi.org/10.37190/ppmp/130795.

[33] S.J.S. Chelladuri, K. Murugan, A.P. Ray, M. Upadhyaya, V. Narasimharaj, S. Gnanasekaran, Mater. Today: Proc. 37(2) (2021) 1301–1304. https://doi.org/10.1016/j.matpr.2020.06.466.

[34] N. Manmai, Y. Unpaprom, R. Ramaraj. Biomass Convers. Biorefin. 11 (2021) 1759–1773. https://doi.org/10.1007/s13399-020-00602-7.

[35] M. Mourabet, A. El Rhilassi, H. El Boujaady, M. Bennani-Ziatni, R. El Hamri, A. Taitai, Appl. Surf. Sci. 258(10) (2012) 4402–4410. https://doi.org/10.1016/j.apsusc.2011.12.125.

[36] S.L.C. Ferreira, R.E. Bruns, H.S. Ferreira, G.D. Matos, J.M. David, G.C. Brandao, E.G.P. da Silva, L.A. Portugal, P.S. dos Reis, A.S. Souza, W.N.L. dos Santos, Anal. Chim. Acta 597(2) (2007) 179–186. https://doi.org/10.1016/j.aca.2007.07.011.

[37] E.K. Tetteh, S. Rathilal, Bioengineering 9(3) (2022) 95. https://doi.org/10.3390/bioengineering9030095.

[38] N.P. Sibiya, G. Amo-Duodu, E.K. Tetteh, S. Rathilal, Sci. Afr. 17 (2022) e01282. https://doi.org/10.1016/j.sciaf.2022.e01282.

[39] W. Salah El-Din Mohamed, M.T.M.H. Hamad, M.Z. Kamel, Water Environ. Res. 92(7) (2020) 1080–1088. https://doi.org/10.1002/wer.1305.

[40] A. Masmoudi-Soussi, I. Hammas-Nasri, K. Horchani-Naifer, M. Ferid, Int. J. Miner. Process. 123 (2013) 87–93. https://doi.org/10.1016/j.hydromet.2020.105253.

[41] Z. Li, G.P. Demopoulos, J. Chem. Eng. Data 50(6) (2005) 1971–1982. https://doi.org/10.1021/je050217e.

[42] Z. Li, G.P. Demopoulos, J. Chem. Eng. Data 51(2) (2006) 569–576. https://doi.org/10.1021/je0504055.

[43] L. Fornsten, Biomaterials 19(6) (1998) 503–508. https://doi.org/10.1002/tqem.21929.

CEMRE AVŞAR[1,2]
SUNA ERTUNÇ[2]

[1]Toros AGRI Industry and Trade Co. Inc. R&D Center, Mersin / Turkey

[2]Ankara University, Department of Chemical Engineering, Ankara/ Turkey

NAUČNI RAD

UKLANJANJE FLUORIDA IZ FOSFOGIPSA: PREDINDUSTRIJSKA STUDIJA I NJENA MATEMATIČKA ANALIZA

Ova studija govori o efikasnosti uklanjanja fluorida iz fosfogipsa na matrici eksperimenta u laboratoriji dizajniranoj Boks-Benkenovim planom. Temperatura, odnos čvrsta/tečnost i vreme utiču na efikasnost uklanjanja fluorida iz fosfogipsa pomoću rastvora različitih soli. Eksperimentalne matrice su dizajnirane prema tipovima rastvora soli: morska voda, 5% NaCl i 10% rastvori NaCl. Analiza faktor-odgovor je pokazala direktnu proporcionalnost između efikasnosti uklanjanja fluorida i temperature. Optimalni uslovi uklanjanja fluorida su određeni softverom Design Expert v.12. Optimalna temperatura, vreme i odnos čvrsta/tečnost bili su 80 °C, 3 h i 0,174 za morsku vodu. Softver je predvideo efikasnost uklanjanja fluorida od 73,31% pri optimalnim uslovima, dok je eksperimentalna vrednost bila 74,99%. Pošto se stvarna i predviđena efiksanost uklanjanja dobro slažu, postupak bi moga biti koršćen kada je potrebno uklanjanje fluorida na industrijskom nivou do unapred određenog nivoa pre određene upotrebe fosfogipsa. Ova studija pruža novi postupak za uklanjanje fluorida na preindustrijskom nivou, posebno za industriju đubriva i cementa. Fosfogips ima veliki potencijal kao alternativna sirovina, a uklanjanje fluorida može biti važno u primenama reciklaže.

Ključne reči: fosfogips, uklanjanje fluorida, Boks-Benkenov dizajn, metodologija odzivne površine.