



Removal of paraquat from synthetic wastewater using phillipsite–faujasite tuff from Jordan

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ARTICLE INFO

Article history:

Received 17 April 2008

Received in revised form 16 June 2008

Accepted 17 June 2008

Available online 4 July 2008

Keywords:

Faujasite

Paraquat

Wastewater treatment

Jordan

ABSTRACT

A phillipsite–faujasite tuff (faujasite) from Jordan has been activated and characterized to evaluate its efficiency in removing paraquat from synthetic wastewater and to specify optimum conditions with maximum efficiency of the faujasite tuff. Noticed variation in CEC is indicated and explained by selectivity of the faujasite to K^+ and Na^+ . Removal of paraquat by using faujasite directly gave average removal efficiency equal to 59%. Thermal activation of the samples enhances their performance. The higher is the temperature of activation the higher the efficiency. Treatment of paraquat effluent using faujasite is a good alternative. Na- or K-loading of the original sample give better results. Loading with Ca and Mg however is not recommended because they always exhibit lower efficiency, which might be related to their lower CEC value. Removal of paraquat from wastewater using charcoal and the non-activated faujasite increased efficiency to about 82%. Thermal activated faujasite at 200 °C and 300 °C increased the uptake up to about 93% and 99.5%, respectively. Therefore thermal activation of faujasite is necessary to improve its uptake performance.

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1. Introduction

Water is the most valuable limited resources especially in Jordan. Hence, Jordan has come to rely increasingly on wastewater treatment, and its reuse to compensate scarcity in water resources. With industrial advances, chemical and bacteriological contaminations of water stream have become an issue of worldwide concern. Many of pesticides are toxic. However, it is impossible to eliminate these chemical substances from the environment, as long as the use of pesticides continues on its current path. Therefore, it is necessary to limit the chemical substances discharged into the environment as much as possible, and also to act on removing them completely. Several treatment methods of wastewater have been reported to remove toxic or volatile organic compounds which are xenobiotic. The photochemical decomposition of organic compounds such as residual pesticides in the environment by ultraviolet irradiation using titanium dioxide (TiO_2) as photocatalyst is a promising method of water purification [1,2]. Decomposition by ozonation, or alkaline hydrolysis have also been used [3]. The adsorption on clay minerals and zeolites is very good method for wastewater treatment [4,5].

Pesticides are generated from agricultural and veterinary factories and industries. The Veterinary and Agricultural Products Manufacturing Company (VAPCO), which is the case study in this project, is one of 14 such industries in Jordan. The VAPCO factory processes produce 1–2 m³/day of wastewater, highly polluted with pesticides and other toxic organic compounds [2]. There are about 200 different products manufactured by VAPCO. Paraquat was chosen because it is water soluble, highly stable, and heavily produced by VAPCO [5]. Paraquat effluent comes from washing the machinery and factory floor after each patch production. Concentration of paraquat in the effluent is estimated to be 0.5%. Paraquat is the trade name for *N,N'*-dimethyl-4,4'-bipyridinium dichloride, which is also referred to as methyl viologen [6]. According to Tomlin [7], paraquat is stable in neutral and acidic media, but readily hydrolyzed in alkaline media and its solubility in water at 20 °C is 620 g/l.

Paraquat is a non-selective quaternary nitrogen herbicide highly toxic for both animals and humans [8]. Thousands of deaths occurred after ingestion (in humans often suicidal) or dermal exposure to paraquat [9]. Both in acute and chronic intoxication primary injuries to mammals occur in the lungs, which selectively accumulate paraquat [10]. Since there are no known pharmacological antagonists of paraquat and no chelating agents capable of binding the poison in the blood or other tissues, the management of paraquat poisoning has been directed towards the modification of the toxicokinetics of the poison by decreasing the absorption or decreasing the oxidant-induced cellular damage [11]. Zeolites

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have been evaluated by Walcarius and Mouchotte [12] for its ability to durably immobilize the paraquat in conditions simulating acute poisoning by oral ingestion of this toxic compound. Walcarius and Mouchotte [12] concluded that zeolites are promising primary treatment of acute paraquat poisoning.

Crystalline zeolites including faujasite are unique adsorbent materials characterized by void volumes of 18–50% [13]. The experimental and the calculated surface area values of faujasite type structure may range between 903 and 1132 m²/g [14]. A prerequisite condition for faujasite to act as adsorbents is that the zeolites first be hydrated by heating and/or evacuation. Natural zeolites possess a high affinity for water and have capability of adsorbing or desorbing water molecules without damaging the crystal structure [15]. According to Breck [16], the selectivity of adsorption depends mainly on the polarity, shape and size of the diffusing molecules relative to the geometry of the zeolites opening; the presence of exchangeable cations and impurities in the zeolite structure and the chemical and physical treatments of zeolites.

Natural zeolitic tuff is widely available at low cost in Jordan [17]. The Jordanian phillipsite–faujasite tuff from Jabal Hannoun volcanoes has suitable properties that enable it to be used for ion exchange processes [18]. These include suitable grain size and total cation exchange capacity, acceptable zeolite content, good attrition resistance and high packed-bed density [19,20]. The phillipsite–faujasite tuff from Jabal Hannoun was selected to be part of a wastewater treatment plant to treat industrial effluent from the VAPCO [2,4,5]. Detailed description of the geology and mineralogy of the studied phillipsite–faujasite tuff is reported in Ibrahim and Hall [21]. The present aim is the evaluation of the Jordanian-activated (thermally and chemically) and non-activated natural phillipsite–faujasite tuff in the removal of paraquat from synthetic wastewater. The purpose is to specify optimum conditions with maximum efficiency of the phillipsite–faujasite tuff.

2. Materials and methods

A representative phillipsite–faujasite tuff bulk sample weighing about 100 kg was collected from the eastern flank of Jabal Hannoun volcano. Sample was subjected to grinding and sieving. Following the mineral processing, the sample was subjected to characterization following the procedures of Ibrahim [19]. Zeolite content was calculated using X-ray diffraction techniques as recommended by Ibrahim and Inglethorpe [22]. According to Ibrahim [19], the zeolite sample which has the particle size between 1.00 mm and 0.425 mm represents samples with high grade and yield. The bulk sample with particle size between 1.00 mm and 0.425 mm will be referred to hereafter as (F). Several samples weighing about 50 g each were chemically activated by soaking at 80 °C with 200 ml of 0.5 M solution of CaCl₂, KCl, MgCl₂ or NaCl to produce Ca–F, K–F, Mg–F and Na–F forms, respectively. Small portion of the original sample (F) and the chemically activated forms were subjected to thermal activation by combustion under 200 °C and 300 °C for 2 h. The samples (F, Ca–F, K–F, Mg–F and Na–F) were characterized to verify their chemical and technical specifications. Water adsorption capacity and percent of water dehydrated were measured at temperature range from 100 to 600 °C. Cation exchange capacity (CEC) was determined following Mercer and Ames [23]. The exchanged cations have been determined using atomic absorption spectrophotometer with calibration curve for each element.

Five liters of simulated wastewater effluent was prepared in the lab. The starting concentration for paraquat was 49 ppm, which gives a TOC value equal to 29.85 ppm. It was treated by the phillipsite–faujasite tuff using two routes (Fig. 1). Route one represents direct contact of the wastewater effluent with the F sample or the chemically and thermally activated F forms. The second route

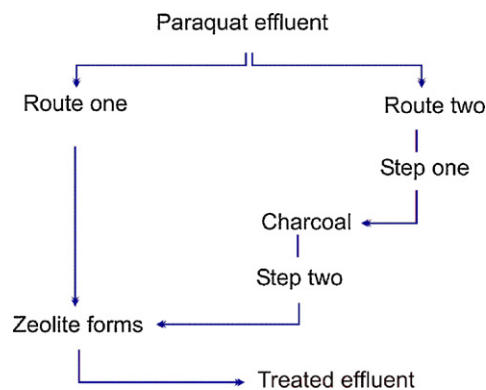


Fig. 1. Flow chart of paraquat treatment.

consists of two steps; step one was pretreatment of the effluent by charcoal followed by step two which comprises treatment with F sample or the thermally activated F forms. Comparison between the efficiency of the chemically and thermally activated faujasite using the two routes was carried out. The TOC content of the analyzed samples containing pesticide were measured by indirect methods by taking the difference between the total carbon (TC) and the inorganic carbon (IC) using Shematsu TOC–V_{CPN} instrument. The system includes an autosampler ASI-V and an NDIR detector.

In route one which represents direct contact of the wastewater effluent with the original sample and the modified forms, 50 ml of the effluent was added to 0.25 g of the adsorbent in 100 ml screw cap flasks. The flasks were kept in a thermostatic shaker at 25 °C for 72 h to reach equilibrium. Each suspension was then filtered, and the TC and IC of each sample were measured (reproducibility is 1.5%). In order to ensure the reliability of the data, a blank was prepared and handled in parallel for each adsorption test. Potassium hydrogen phthalate (KHP) was used as a standard for TC calibration and NaHCO₃ for IC calibration.

In the first step of route two (Fig. 1), a 0.6 g weight from industrial charcoal was shaken at 25 °C for 72 h with 300 ml of wastewater. The suspension was then filtered, and the TOC values of each sample were measured using TOC-instrument. The uptake experiment of the pretreated solutions was repeated. These pretreated wastewater samples were subjected to secondary treatment by faujasite using the same methodology used in route one.

3. Results and discussion

X-ray diffractogram of the original sample prior to mineral processing (Fig. 2) indicates presence of faujasite, phillipsite and calcite. Detailed mineralogical study of the sample after mineral processing indicates presence of about 65% of zeolites (45% faujasite and 20% phillipsite), 30% palagonite and about 5% calcite. Zeolites and calcite occur as cement and filling cavities inside volcanoclastic material. Faujasite occurs as octahedral micro-sized crystals with spinle twinning [19] as shown in Fig. 3.

Methylene blue dye was used to estimate the surface area of the five forms of zeolite; the adsorption isotherm data obtained was analyzed using Langmuir isotherms models [24]. The experimental values of the maximum adsorption capacity for the adsorbent (Q_m) and the surface area (S) are shown in Table 1. These values are determined from adsorptive capacity (Q_e) vs. equilibrium concentration (C_e) plot. In detail, Q_m value indicates that F has the highest ability to adsorb methylene blue while K–F has the lowest one. Ca–F and Mg–F have almost the same value, which was greater than Na–F. CEC varies from 152 mequiv./100 g in Ca–F to 216 mequiv./100 g in K–F, whereas, the surface area varies between 113 m²/g in K–F and

Table 1
Specification of the original faujasite tuff sample and the chemically activated forms

Specification	Faujasite forms				
	F	F–Ca	F–K	F–Mg	F–Na
Q_m^a of methylene blue (mg/g)	126.67	99.17	50.10	98.02	70.54
CEC ^b (mequiv./100 g)	178	152	216	168	178
Water adsorption capacity % at 200 °C	6.9	6.5	7.2	7.3	6.5
Water adsorption capacity % at 300 °C	7.9	8.4	8.4	8.0	8.0
Dehydration % at 200 °C	9.2	7.9	8.2	9.2	7.6
Dehydration % at 300 °C	10.8	9.1	8.9	9.7	9.9

^a Q_m = maximum adsorption capacity.

^b CEC = cation exchange capacity.

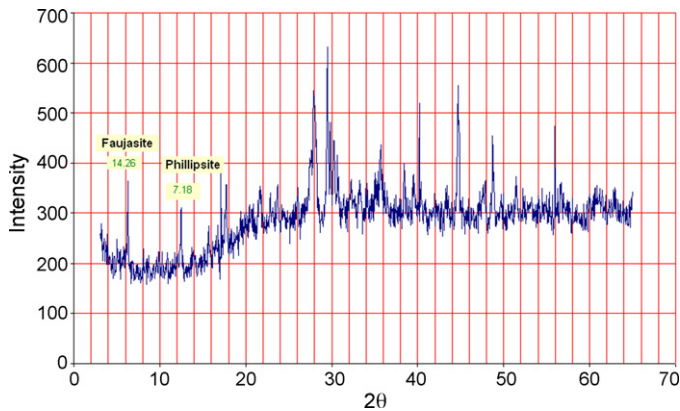


Fig. 2. X-ray diffractogram of the phillipsite–faujasite tuff sample from Jabal Hannoun.

286 m²/g in F. These variations are most probably related to selectivity of the faujasite minerals to the exchangeable cations inside the faujasite structure, which is controlled by the ionic radius and charge.

Dehydration property of the five faujasite forms was examined under a temperature range from 100 °C to 600 °C. As illustrated in Fig. 4, it varies along this temperature range between 4.73% and 11.26%. The dehydration curves for the faujasite forms shown in Fig. 2 indicate that the maximum water loss is found in the F which is about 12% occurring closed to 500 °C. Both Ca–F and K–F have a maximum water loss of 10% occurs at 400 °C; while Na–F has the

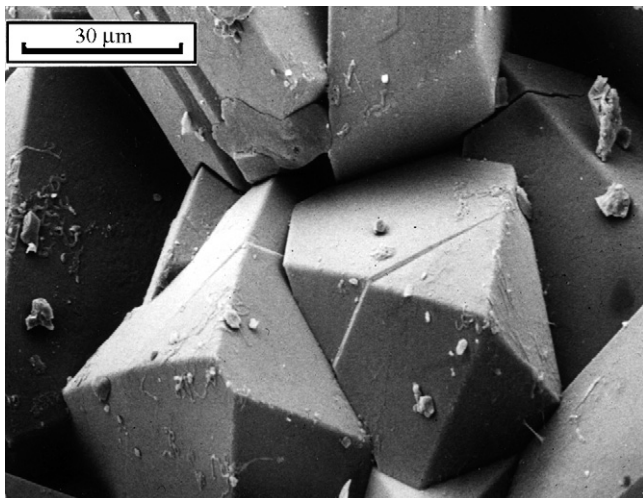


Fig. 3. Scanning electron micrograph of faujasite from Jabal Hannoun [19].

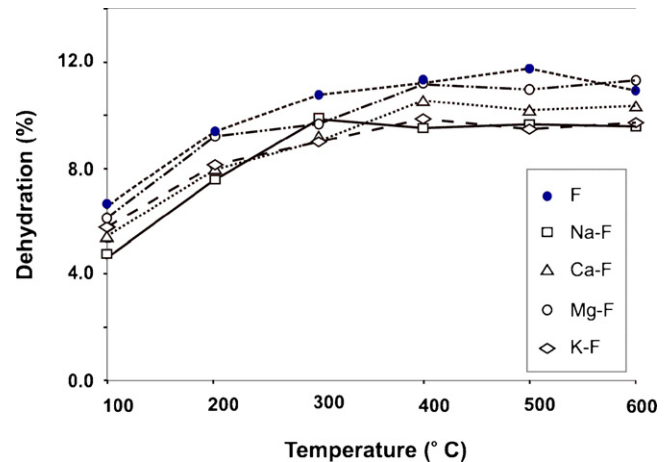


Fig. 4. Dehydration curves of the faujasite forms at temperature range between 100 °C and 600 °C.

same value of water loss but occurs at 300 °C. Furthermore, Mg–F has a maximum of 11% occurring at 400 °C.

The water adsorption capacity of the faujasite forms at 200 °C and at 300 °C as illustrated in Table 1 is 6.5–7.2% and 7.9–8.4%, respectively indicating narrow variations (0.7% and 0.5%, respectively). The percentage of dehydration of the faujasite forms is always (0.5–2.9%) higher than that of the percentage of hydration (see Table 1). The variation in the dehydration, among the different forms at 200 °C is 1.2%, and at 300 °C is 1.9%.

Faujasite has a three-dimensional structure with 7.4 Å diameter window openings connecting 13 Å diameter super-cages [25]. According to Walcarius and others [26], paraquat which has a dimension of 13.4 Å × 6.4 Å × 3.4 Å [27] can be readily ion exchanged into the faujasite.

An adsorption isotherm experiment was carried out to estimate the maximum quantity of paraquat that can be adsorbed on the surface of adsorbents (Q_m). The Q_m values for the paraquat on the faujasite forms are given in Table 2. The Q_m value in F is 4.67 mg/g (Table 2), chemical activation of zeolite gives an increase in the Q_m value, mainly for the Na–F and K–F forms to about 7 mg/g. These

Table 2
 Q_m concentration of paraquat (mg/g) in the effluent

Faujasite forms	Specification, Q_m (mg/g)
F	4.67
F–Ca	3.67
F–K	6.96
F–Mg	3.49
F–Na	7.02
Average	5.16

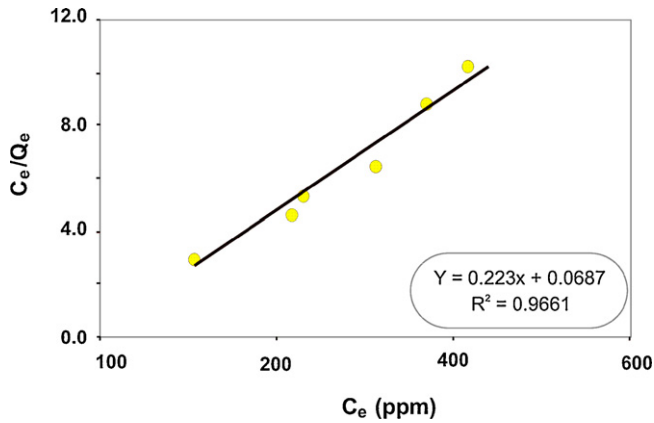


Fig. 5. Adsorption isotherm of paraquat using original faujasite sample.

results are in agreement with Clark [28] that shows an increase in zeolites adsorption with the uniformity of the zeolite structure (all sites of the same crystallographic type constitute one site group, and therefore, many kinds of sites are occupied). The Q_m values of the Ca–F and Mg–F forms is 3.67 mg/g and 3.49 mg/g, respectively. This decrease might be related to adsorption selectivity. The adsorption isotherm of paraquat is shown in Fig. 5.

Removal of paraquat by applying route one gives acceptable results. In detail, efficiency of faujasite and the activated forms in removing the paraquat from the wastewater effluent at room temperature (25 °C) is variable. The TOC values in the treated effluent vary from 48% to 35% (14.32–10.44 ppm) with an average TOC equal to about 41% (12.23 ppm) compared with 100% in original influent (29.84 ppm). This indicates that removal efficiency is between 52% and 65%. Best result was obtained from Na–F (Fig. 6). The trend in efficiency is Na–F > K–F > F > Mg–F > Ca–F. Thermal activation of the faujasite forms at 200 °C enhanced their efficiency to remove paraquat from the wastewater effluent. The efficiency of K–F, which exhibits highest efficiency, increased from 63% to 75%, i.e. efficiency increased about 119% in the K–F, whereas it increased in the F form about 121%. The trend in efficiency is slightly different from that of non-thermally activated forms (K–F > Na–F > Mg–F > Ca–F). The increase in temperature of thermal activation further enhanced performance of the faujasite forms. In detail, thermal activation at 300 °C leads to an average increase in removal efficiency to about 81% in all F forms equal to about 137%. The thermal activated and non-activated Ca–F and Mg–F forms always exhibit lower efficiency compared with Na–F, K–F and F. It can be noted from Table 1 that these two forms have lower CEC values, which influence their removal efficiencies. This might also be related to selectivity of fau-

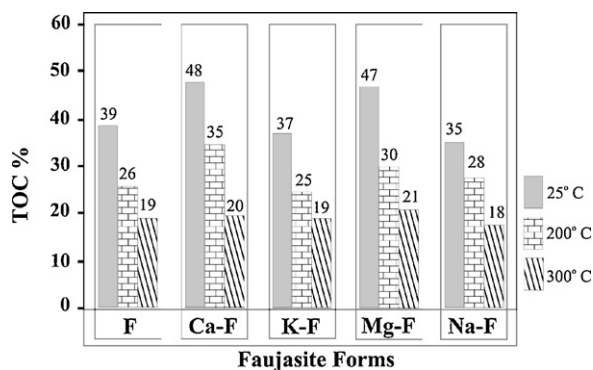


Fig. 6. Efficiency of faujasite and its thermally activated forms in paraquat removal (TOC in the original samples = 29.85 ppm).

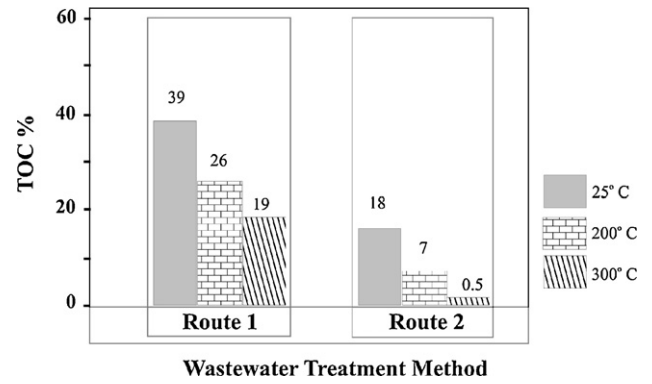


Fig. 7. Faujasite performance during wastewater treatment using route one and route two.

jasite to Ca and Mg is higher selectivity of faujasite to paraquat. It can be concluded from the experiments of route one that treatment of paraquat effluent using F sample is a good alternative. Na- or K-loading of the original sample give better results. Loading with Ca and Mg is not recommended. Thermal activation of the samples enhances their performance. The higher is the temperature of activation the higher the efficiency.

When route two was applied to paraquat effluent, better results were obtained. As shown in Fig. 7, the removal percent of paraquat increased. The TOC decreased in the treated wastewater by using the non-activated F from 39% to 18% indicating increase of uptake from 61% to 82%. The thermally activated F forms show noticed improvement in the efficiency. The TOC values in the treated wastewater were 2 ppm and 0.15 ppm using the F form that has been activated at 200 °C and 300 °C, respectively. That is the removal of paraquat from wastewater increased up to about 93% and 99.5%, respectively. These results indicate that thermal activation of faujasite tuff is necessary to improve its uptake performance of paraquat from wastewater. They also indicate that if the starting wastewater effluent contains high concentrations of paraquat, pretreatment with charcoal is recommended to lower paraquat content in the effluent prior to treatment with faujasite. However if paraquat content in the original wastewater effluent is low, it can be successfully treated directly with faujasite.

4. Conclusions

A faujasite tuff from Jordan containing about 44% faujasite has been chemically and thermally activated. Characterization of the technological parameters of the chemically activated forms indicates noticed variations, mainly in the values of CEC and surface area. But narrow variation in water adsorption capacity of the faujasite forms at 200 °C and at 300 °C. Highest CEC value was registered by K-form indicating higher selectivity of the faujasite minerals to K^+ .

Removal of paraquat by applying route one gives acceptable results, where average removal efficiency equal to 59% is achieved in the samples without thermal activation. Thermal activation at 200 °C enhanced their efficiency to an average of 71%. The increase in temperature of thermal activation at 300 °C further enhanced performance of the faujasite forms to an average increase equal to 81%. The trend in efficiency show slight variations. It always emphasizes that Ca–F and Mg–F forms always exhibit lower efficiency compared with Na–F, K–F and F, may be due to their lower CEC value or selectivity of faujasite to Ca^{2+} and Mg^{2+} higher than selectivity to paraquat. Therefore chemical activations using Ca^{2+} and Mg^{2+} is not recommended.

The TOC% decreased in the treated wastewater by using charcoal and the non-activated F to 18% indicating increase of uptake to 82%. Removal of paraquat from wastewater increased up to about 93% and 99.5% using the thermally activated F forms at 200 °C and 300 °C, respectively. Therefore thermal activation of faujasite tuff is necessary to improve its uptake performance of paraquat from wastewater. If the starting wastewater effluent contains high concentrations of paraquat, pretreatment with charcoal is recommended to lower paraquat content in the effluent prior to treatment with faujasite. However if paraquat content in the original wastewater effluent is low, it can be successfully treated directly with faujasite.

Acknowledgments

This paper is part of an entrepreneurial project funded by the Higher Education Development Fund (HEDF), the Hashemite University (HU) & the Veterinary & Agricultural Products Manufacturing Company (VAPCO). The second author thanks the HU for the M.Sc. studentship that made part of this project possible. Miss Enas Nabih is thanked for assistance with data analysis.

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