Low-Cost Pre-Treatment of Pharmaceutical Wastewater

A. Abu-Safa, S. Abu-Salah, M. Mosa, and S. Gharaibeh

Abstract—Pharmaceutical industries and effluents of sewage treatment plants are the main sources of residual pharmaceuticals in water resources. These emergent pollutants may adversely impact the biophysical environment. Pharmaceutical industries often generate wastewater that changes in characteristics and quantity depending on the used manufacturing processes. Carbamazepine (CBZ), {5H-dibenzo [b,f]azepine-5-carboxamide, $(C_{15}H_{12}N_2O)$}, is a significant non-biodegradable pharmaceutical contaminant in the Jordanian pharmaceutical wastewater, which is not removed by the activated sludge processes in treatment plants. Activated carbon may potentially remove that pollutant from effluents, but the high cost involved suggests that more attention should be given to the potential use of low-cost materials in order to reduce cost and environmental contamination. Powders of Jordanian non-metallic raw materials namely, Azraq Bentonite (AB), Kaolinite (K), and Zeolite (Zeo) were activated (acid and thermal treatment) and evaluated by removing CBZ. The results of batch and column techniques experiments showed around 46% and 67% removal of CBZ respectively.

Keywords—Azraq bentonite, carbamazepine, pharmaceutical wastewater, zeolite.

I. INTRODUCTION

THIS paper presents the results of a research aimed at studying the efficiency of non-metallic raw materials in removing CBZ from the pharmaceutical wastewater.

Jordan comes fourth in ranking categorizing the most water-deprived countries, due to the limited available water resources, which necessitates that more efforts shall be considered in the area of water conservation and environment protection. In pharmaceutical industries in Jordan, wastewater is mainly generated by washing activities of the equipment. Pharmaceutical and Personal Care Products (PPCPs), which have potential impacts on the receiving environment, are poorly studied.

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"Reference [1] shows that CBZ is not removed by the activated sludge processes in treatment plants, whereas, other wastewater treatment methods remove low percentages of CBZ".
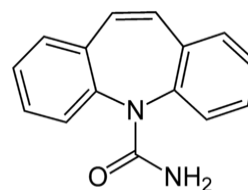

Fig. 1 Chemical structure of carbamazepine

With increasing environmental concerns, non-metallic raw materials, which are porous crystalline substances, have recently attracted much attention and increasing interest due to their promising use in water and wastewater treatment. Adsorption technique through non-metallic raw materials has been investigated to be a useful alternative to the conventional treatment methods for the removal of heavy metals and toxic organic pollutants from water and wastewater.

So, this study can be considered as a first step into thinking of application of adsorption technique by using the low-cost local activated non-metallic raw materials to remove the most toxic pharmaceutical pollutants from the wastewater in Jordan. Also, the current study is vital to prognose the economic benefits of Jordanian non-metallic raw materials in industrial applications.

II. EXPERIMENTAL WORK

Jordanian non-metallic raw materials (reagents) were provided by the Natural Resources Authority (NRA). These reagents were purified and separated from non-clay materials in a Mozely-hydrocyclone. Only clay particles ≤ 63 μm in size were used. Chemicals (indicators, hydrochloric acid, boric acid, sulphuric acid, hydrofluoric acid, benzene, and n-butylamine) and powder activated carbon (particle size < 100 μm, plant source) were purchased from Merck (Germany). Pure CBZ substance was obtained from Jordanian pharmaceutical factory.

Clay Pre-treatment

Acid Treatment: 0.50 g of reagents were boiled separately with 50 cm³ of hydrochloric acid or sulphuric acid with concentration of 0.1 M or 1.0 M for 30 minutes, then filtered under vacuum and washed with distilled water. The acidified reagents were dried overnight at 80 °C.

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Thermal Treatment (calcination): The acidified reagents were placed in a furnace at a temperature of 250 ^{o}C for 60 minutes.

Method of Characterization

Surface Acidity: Non-aqueous titration technique was applied to measure the surface acidity of the reagents using n-butylamine as a titrant and indicators with different pKa values to determine the number of acidic sites (Brönsted and Lewis sites). A border range of indicators with different pKa values was used to measure the surface acidity of the reagents. The acid amount indicated by using methyl red indicator (pKa = 4.8), is the amount of acidic sites having the acid strength of $H_o < 4.8$ (H_o is a measure of the acid strength, the smaller H_o value, the stronger acid strength). By using various indicators of different pKa values like methyl orange (pKa = 3.6), bromocresol green (pKa = 2.9), and thymol blue (pKa = 1.2), it is possible to titrate the centres at various acidic strength distribution.

0.10 g of reagents suspended in benzene were titrated with 0.001 M n-butylamine, indicators with different pKa values (methyl red, methyl orange, bromochresol green, and thymol blue) were used [2].

Surface Area Measurement: Methylene blue surface area method was carried out to calculate the accessible surface area which is available in the reagents [3].

Mineralogical Investigation: Scanning electron microscopy (SEM model FEI Quanta 200) was used to identify the shape and texture of mineral constituents in laboratory of Earth and Environmental Sciences Department at Yarmouk University. X-ray diffraction (XRD) of reagents were accomplished in the laboratory of Faculty of Archaeology and Anthropology at Yarmouk University by using (XRD 6000 instrument SHIMADZU) to identify the mineral constituents of reagents.

Pharmaceutical Wastewater Samples

Untreated pharmaceutical wastewater samples containing CBZ (concentration of CBZ 3, 3.25, 3.45, 4, 4.29, 6.9, and 7.00 mg/l) were collected from Jordanian pharmaceutical factory. The collected samples were analyzed duplicate before and after treatment by activated reagents.

The analytical procedure of CBZ was based on a previously reported validated method for the determination of CBZ using RP-HPLC method [1].

Standard stock solutions of CBZ were prepared with methanol. Calibration graphs were prepared using peak area and the concentrations of samples in a mobile phase. The concentration of CBZ in the samples was calculated by comparison with peak area obtained from standard stock solutions.

Batch Technique

A 1000 ml of pharmaceutical wastewater samples with a known weighed reagents were placed in each Jar test beaker and mixed. After stirring the samples with the reagent, the contents were left to let the pollutants adsorbed onto the reagent to settle out. Efficiency of the experimental reagents was evaluated by measuring CBZ concentration.

The optimum operation conditions of the experiment were determined during the experiments.

Column Technique

Continuous flow fixed-bed column was applied to study the efficiency of the AB, K, and Zeo to remove CBZ from pharmaceutical wastewater. The optimum operation conditions (flow rate, bed depth, and column internal diameter) were determined during the experiments.

III. RESULTS AND DISCUSSION

Effect of Acid Treatment on Surface Acidity and Surface Area

When some reagents (clay) are treated with acids, protons released replace the cations on the interlamellar surfaces of the reagent. This decationation leads to an increase in the number of acidic Brönsted sites. However, in case of AB, whose major constituent is montorillonite, an enhancement of catalytic activity due to decationation is not expected. This is due to the fact that montmorillonite is octahedrally charged at which silicate is substituted by Mg^{2+} in the octahedral sheets and substituted very limited by Al^{3+} in the tetrahedral sheet. Consequently, the released protons will migrate via the hexagonal hole and become attached to the OH-group located below the hole producing Brönsted acid sites ($—OH_2^+—$) [4].

The acid treatment of the clay is expected to increase its activity for adsorption process, because it increases the acidity of the clay surface by replacing its exchangeable cations by protons, and by increasing the percentage of aluminum in the tetrahedral sheet in phyillosilicate, which gives high cracking activity. However, higher level of acid concentration leads to the destruction of the crystalline structure of the reagents, so the surface acidity will decrease due to loss of many active acid sites. In fact, dealumination by acid treatment must be kept below 50% to ensure that the activation of the reagents by acid treatment is not reduced [5].

"Reference [6] shows that the acidic strength of acidic sites in kaolinite was found stronger than acidic strength of acidic sites in montmorillonite. In addition, monmorillonite contains a larger number of weaker acidic sites compared to the number of stronger acidic sites in kaolinite".

Table I shows the surface acidity of the different reagents, which were used in the experiments. A maximum number of weaker acidic sites ($H_o < 4.8$; H_o *is a measure of the acid strength*) was obtained when AB was treated with 0.1 M HCl or 1 M H_2SO_4, due to the fact that, when clay is treated with lower acid concentration, aluminum ions in six-fold coordination go faster into four-fold in the tetrahedral sheet layers, increasing the percentage of aluminum in the tetrahedral sheet, thus promoting the catalytic activity by increasing the number of acidic sites on the surface [7]. As the concentration of acid is increased above 1.0 M, the amount of Al_2O_3 removed from the tetrahedral sheet will increase, leading to a loss of acidic sites centers on the clay surfaces. The maximum number of acidic sites ($H_o < 2.9$) was obtained when K was treated with 1.0 M H_2SO_4. The maximum number of stronger acidic sites ($H_o < 1.2$) was obtained when Zeo was treated with 1.0 M H_2SO_4.

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TABLE I
SURFACE ACIDITY OF NON-METALLIC RAW MATERIALS

Clay	Acid treatment followed by thermal treatment at 250 °C	Concentration (mol/L)	Surface acidity (mmol H^+ / g of clay)			
			(*) $H_O < 4.8$	$H_O < 3.6$	$H_O < 2.9$	$H_O < 1.2$
Zeolite	HCl	C^*	0.040	0.030	0.030	0.074
		0.1	0.075	0.128	0.046	0.030
		1.0	0.030	0.038	0.040	0.021
	H_2SO_4	C^*	0.040	0.030	0.030	0.074
		0.1	0.050	0.070	0.058	0.011
		1.0	0.064	0.260	0.260	0.264
Azraq Bentonite II	HCl	C^*	0.023	0.020	0.021	0.019
		0.1	0.356	0.290	0.110	0.022
		1.0	0.330	0.220	0.099	0.013
	H_2SO_4	C^*	0.023	0.020	0.021	0.019
		0.1	0.310	0.073	0.156	0.160
		1.0	0.350	0.226	0.200	0.100
Azraq Bentonite I	HCl	C^*	0.028	0.025	0.012	0.030
		0.1	0.395	0.343	0.148	0.053
		1.0	0.380	0.240	0.112	0.070
	H_2SO_4	C^*	0.028	0.025	0.012	0.030
		0.1	0.340	0.151	0.158	0.170
		1.0	0.400	0.292	0.202	0.110
Kaolinite	HCl	C^*	0.050	0.050	0.100	0.010
		0.1	0.060	0.080	0.048	0.044
		1.0	0.068	0.090	0.032	0.038
	H_2SO_4	C^*	0.050	0.050	0.100	0.010
		0.1	0.050	0.065	0.128	0.078
		1.0	0.070	0.080	0.228	0.052

(*) H_O: Hammet acidity function = (pKa: equilibrium dissociation constant of acid) + (logarithm of molar concentration of neutral base or conjugate acid).
C^*: Control sample.
Azraq Bentonite I and Azraq Bentonite II are different in location and depth of reserve.

The specific surface area is a highly significant parameter in nearly all physical and chemical processes involving powdered solids. The accessible surface area of reagents was calculated at different concentrations of methylene blue to measure the amount of methylene blue adsorbed onto surface area of the reagents using the following equations:

$$(C_s) = (C_{w,i} - C_{w,eq}) \times V \div W \qquad (1)$$
$$(A_s) = (C_{s,max} \times N_A \times MA) \div MW \qquad (2)$$

Equation (1) and (2) represent the calculations of accessible surface area, where; Cs: amount of adsorbed material at equilibrium, $C_{w,i}$: initial concentration of adsorbed material in water, $C_{w,eq}$: equilibrium concentration of adsorbed material remaining in solution after mixing, V: volume of solution, W: oven dry weight of soil.

For the second equation, A_s: accessible surface area, $C_{s,max}$: maximum sorption value, which can be obtained from the relationship between C_s and number of methylene blue moles, N_A: Avogadro's Number, MA: molecular area; it is the effective area per molecule of methylene blue, MW: molecular weight of methylene blue.

Table II shows the surface area of the activated reagents. Activated reagents with acids (0.1 M of HCl or H_2SO_4 at 250 °C) were experimentally found higher than the surface area of untreated reagents. This is due to the fact that Al_2O_3 is leached out from the clay layers (tetrahedral and octahedral sheets) upon acid treatment leading to increase in the porosity and the surface area of the reagents until a critical concentration of acid.

Using high concentration of acids (≥1.0 M of acids) was experimentally found leading to remove a large amount of Al_2O_3 from both tetra and octahedral layers that leads to decrease the porosity and surface area. In addition, collapsing of the crystalline structure of the reagents was taken place [4].

Effect of Thermal Treatment on Surface Acidity and Surface Area

The thermal treatment (calcination) activates the reagents by improving the cation exchange capacity of its minerals by dehydrating the cations and decomposing the organic molecules present between the clay layers.

Although calcination enhances the catalytic properties of reagents, it may have disadvantages when it is performed at rather high temperatures causing a reduction of the porosity, surface area, and surface acidity as a result of the collapse of the crystalline structure of the layers. The clay may also suffer from a loss of some of its acidic sites and form a change in activity due to a redistribution of the remaining acidic sites. In general, a maximum number of acidic sites is obtained upon calcination at 250 °C. This is referred to the dehydration of the reagents at this temperature allowing the indicator molecules to evaluate the acidic sites to reach to the acidic centers. The effective amount of acidic sites would also increase due to dehydroxylation of water molecules. The decrease of acidity upon calcination at higher temperatures is due to the fact that a collapse in clay structure takes place due to the thermal instability of the clay, which leads to decrease in the surface area and consequently a decrease in the number of acidic sites [8].

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TABLE II
SURFACE AREA OF NON-METALLIC RAW MATERIALS

Clay	Acid Concentration	Calculated Accessible Surface Area (m^2/g)
K	control	36.22
	0.1 M HCl	43.59
	1.0 M HCl	23.19
	0.1 M H$_2$SO$_4$	44.52
	1.0 M H$_2$SO$_4$	15.55
Zeo	control	23.59
	0.1 M HCl	34.88
	1.0 M HCl	24.16
	0.1 M H$_2$SO$_4$	24.00
	1.0 M H$_2$SO$_4$	24.12
AB I	control	59.66
	0.1 M HCl	60.33
	1.0 M HCl	48.00
	0.1 M H$_2$SO$_4$	60.39
	1.0 M H$_2$SO$_4$	12.26
AB II	control	84.34
	0.1 M HCl	60.54
	1.0 M HCl	48.18
	0.1 M H$_2$SO$_4$	48.29
	1.0 M H$_2$SO$_4$	24.28

K: kaolinite, Zeo: zeolite, AB I: Azraq Bentonite, and AB II: Azraq Bentonite

Scanning Electron Microscopy (SEM)

Fig. 2 and Fig. 3 represent the shape and texture of phillipsite rods of natural zeolite before and after activation.
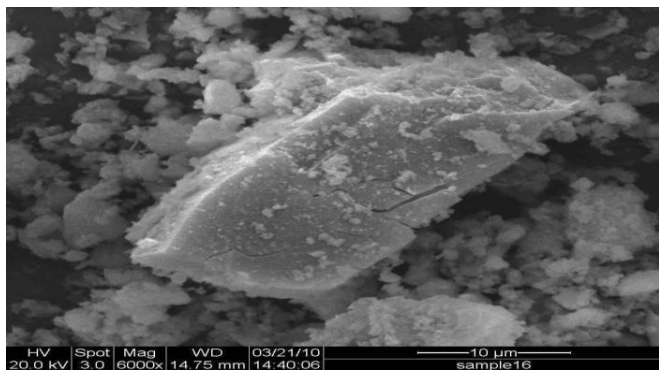

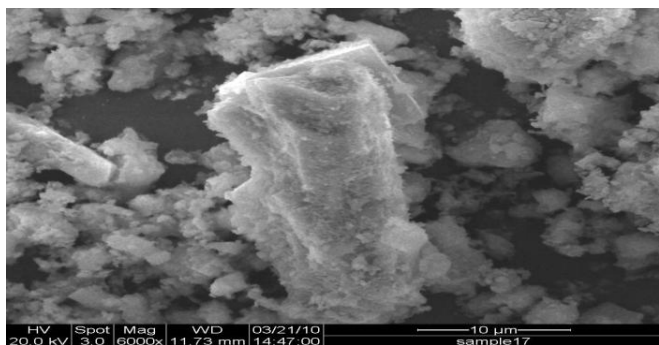Fig. 2 Phillipsite rods of zeolite before activation

Fig. 3 Affected Phillipsite rods of zeolite after activation

Batch Technique Results

A 1000 ml of pharmaceutical wastewater samples with a known weighed reagents (1g or 2g) were placed in each Jar test beaker and mixed for 60 minutes (contact time) at room temperature (25 ^{o}C). The pH of wastewater sample was 8.53 and the pH of activated reagents ranged from 2.50 to 5.80. After stirring the samples with the reagent, the contents were left for 2 hours for sedimentation to settle out the used reagents with the pollutants from the wastewater sample. After that, the treatment efficiency of the experimental reagents was evaluated by measuring CBZ concentration.

The highest removal efficiency of CBZ from pharmaceutical wastewater was achieved when using 0.1 M of H$_2$SO$_4$ of activated AB II (46%) and 0.1 M of activated K (38%).

It was expected that activated carbon will have the highest removal efficiency of CBZ due to the high surface area of activated carbon in comparison with the surface area of reagents, but it removed only 14% (2g reagent/L pharmaceutical wastewater) and 29% (1g reagent/L pharmaceutical wastewater) of CBZ in pharmaceutical wastewater, which is less than the removal efficiency of 1 g of the AB, K, and Zeo.

Fig. 4 represents the removal efficiency of CBZ using activated reagents. The removal efficiency of CBZ ranges between 1.86% and 46%.
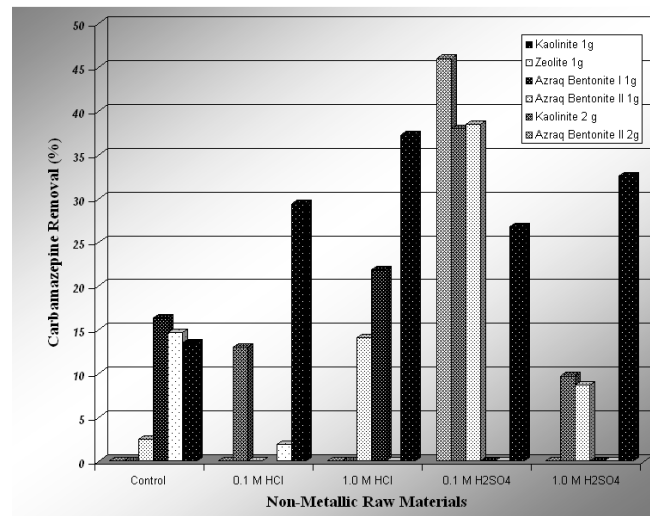

Fig. 4 Efficiency of non-metallic raw materials in removing CBZ

Bentonite has Brönsted acidic sites, which are proton donors (H$^+$), which provides a free space to the functional group of CBZ (amide group), which has a free pair of electrons on the central atom (N) that is not bonding. So, CBZ binds with the proton which leads to the adsorption at the Brönsted acidic sites at the surface layers of the clay.

Column Technique Result

A series of experiments were carried out in glass columns with constant dimensions of inner diameter of 30 mm and height of 270 mm. Columns were filled with the lower gravel layer, sand layer, zeolite layer, and upper gravel layer. The depth of each component of the column was 90 mm, 25 mm, and 60 mm, and 50mm respectively. Column experiments

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were conducted using the down-flow mode through the fixed bed at a constant flow rate of 1 ml/min at room temperature (25 ^{o}C) and acidic media pH (2.50 – 5.80). In all experiments, the samples were collected at the effluent of the column and analyzed for CBZ.

The results of using column experiment indicate that zeolite possesses good results in removing CBZ. The experimental results of different contact times are shown graphically in Fig. 5 by plotting the ((C_{O} $_-$ C/ C_{O}) *100) ratio (C_{O}-concentration of CBZ in influent and C-concentration of CBZ in effluent) versus time.

The best maximum removal efficiency of untreated Zeo (67%) was achieved after 22 hours, and then the efficiency decreased to (36%) after 93 hours from the operation start.
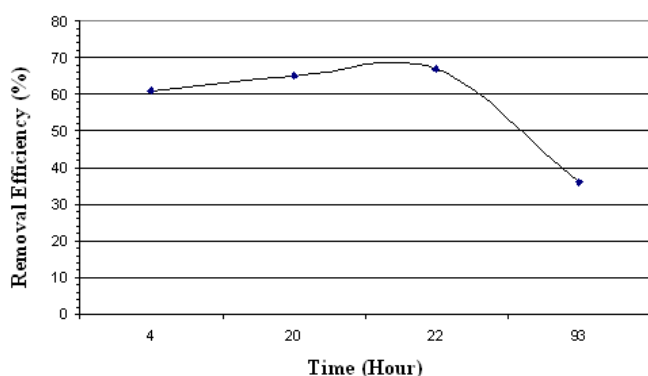

Fig. 5 Effect of contact time on CBZ removal

When clay minerals (AB and K) are added to a small amount of water, the small crystals disperse and separate as a result of their chemical and hydration properties. The electric potential causes the particles to repel each other and stay in suspension as a colloid. The addition of more clay (coagulant) to the water causes the liquid to become viscous, which lead to develop thixotropism. Thixotropy properties results due to the negatively charged basal surfaces and positive charges present at the crystal edges which attract each other. Therefore, thixotropic properties of clay minerals act as a gel-like property, which entraps the liquid and becomes impermeable for water [9]. Therefore, AB and K were not effective in column technique to remove CBZ.

IV. CONCLUSION

Acid treated reagents possess more acidic sites than the untreated reagents.

A maximum number of weaker acidic sites (H_o<4.8) was obtained when AB was treated with 0.1 M HCl or 1 M H_2SO_4. High acid concentration was experimentally found to induce dealumination process in reagents causing the surface area to decrease. Maximum surface acidity was also obtained upon calcination at 250 ^{o}C.

The optimum dose of reagents in batch technique was achieved at 2 g of AB II / L of pharmaceutical wastewater. More than optimum dose of reagents, environmental problems come from treatment sludge could be generated. The increase of contact time between the media of bed depth and CBZ,

leads to better column efficiency until a critical time. After that the column efficiency in removing CBZ starts to decrease.

It is worthy to mention that there is no specific standard related to the allowable concentration limit of CBZ in Jordan, so this research is important as a first step to establish Jordanian specific standard to determine concentration limit of CBZ in effluent of pharmaceutical industries, because the allowable concentration limit in European countries is identified in nanorgam per liter.

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