Stabilization of phenol trapped by agricultural waste: a study of the influence of ambient temperature on the adsorbed phenol

Maha H. Alhassani, Sama M. Al-Jubouri*, Haider A. Al-Jendeel

Department of Chemical Engineering, College of Engineering, University of Baghdad, Aljadria, Baghdad, P.O.Box: 47024, Iraq, email: alhassani_maha@yahoo.com (M.H. Alhassani), sama.al-jubouri@coeng.uobaghdad.edu.iq (S.M. Al-Jubouri), haider.aljendeel@yahoo.co.uk (H.A. Al-Jendeel)

ABSTRACT

This work investigates the efficacy of agricultural waste material in the removal of phenol from aqueous solution. *Ceratophyllum demersum L.* (Al-Shamplan plant) plant widespread grows in the south of Iraq. The influence of local ambient temperature on the releasing of phenol adsorbed from the waste adsorbent was thoroughly investigated. A comprehensive study was conducted in a batch mode by varying contact time, initial phenol concentration and initial pH of phenol solution. Al-Shamplan plant showed a favorable performance as an alternative to costly adsorbent used to remove phenol from aqueous media with a removal efficiency of 94.7%. Also, a study of the ambient temperature effect on liberation of the adsorbed phenol from Al-Shamplan showed that leaching of phenol approximately stopped after 2 d at 50°C. But, phenol leaching continued for 30 d at 20°C. The solidification of phenol was successfully achieved and for the first time using the geopolymerization method, and the feasibility of stabilizing phenol for environment management was demonstrated. Since the phenol leaching to the environment was reduced to 50%. The experimental data are well fitted to the Langmuir isotherm model, and the easy adsorption of phenol by Al-Shamplan plant was proved by the Freundlich isotherm model.

Keywords: Adsorption; Agricultural waste; Phenol; Solidification; Isotherms model

1. Introduction

Industrial processes discharge wastewaters consisting of various types of organic pollutants and refractory compounds which negatively affect the ecosystems [1,2]. Wastewaters resulting from pharmaceutical industry, resin manufacturing, dye manufacturing, oil refineries, pesticides, plasticizers, pulp and paper industry, coal conversion, iron-smelting, textile mills, chemical or petrochemical industries commonly contain high concentrations of phenol (as a major compound) and other phenolic compounds [3–5]. Phenols are poisonous, carcinogenic, low biodegradable compounds. Their presence causes undesirable smell and taste in drinking water even at low concentrations [6].

Also, the presence of phenol groups affects human health, specifically the metabolic activity such as carcinogenicity, endocrine disruptors, and mutagenicity, etc. [7]. When phenolic compounds present in aquatic life, they harm the living organisms and rises the oxygen demand in water sources [6,7]. Wastewater discharged from the above mentioned industries contains a high level of chemical oxygen demand (COD = 10–100 g/L) expressing the content of organic matter, or toxic contaminants. Therefore, direct biological purification processes are impractical and result in dangerous problems in the environment [3]. Also, the too small concentration of these compounds makes profiting their recovery is impractical [5].

* Corresponding author.

To effectively meet the requirements of the environmental regulatory over the last two decades, different thermal, chemical, physical, and biological pre-/post-treatment methods have been improved to eliminate polluting organics in wastewater [3,8]. The allowable concentration of phenol in surface waters as enforced by EPA law is only less than 1 ppb (parts per billion) [9]. The approaches implemented for phenol removal from wastewater can be divided into non-destructive methods including distillation, membrane separation, extraction and adsorption; and distractive methods including oxidation (electrochemical degradation, advanced oxidation processes [6], photocatalysis, wet-air oxidation [10,11]) and biological degradation processes [12,13]. When these treatment techniques have been commonly practiced for the removal of organic contaminants in industrial wastewaters, they showed inherent problems during application [8]. For example, extraction processes require regeneration for the subsequent solvent which increases costs. Separation by membranes is flexible, feasible and consumes low energy but is commonly limited by fouling caused by colloids [12]. Separation processes included within the destructive methods show effective removal of pollutants but they associate with the non-ignorable issue of large energy consumption [14]. Biological methods are cost-effectively, environment-friendly technique, but they are not efficient for non-biodegradable pollutants, toxic contaminants and high concentration of organic pollutants due to biomass poisoning; and the micro-organisms require a long residence time for pollutant degradation [3,4,15].

Adsorption emerges as a common way to remove phenol and other contaminants because of its simplicity of design and operation, low energy cost and high efficiency [16]. Where, various materials have been widely used as adsorbents such as activated carbon, clays, zeolites, mesoporous aluminosilicates, straw, fly ash, automobile tires, coal reject, palm seed coat, biosolids, pistachio nut shell ash, sawdust and fertilizer waste [17,18]. However, adsorption process routinely ends with spent adsorbent containing the displaced non-destructed pollutants. The waste adsorbents are almost considered as hazardous materials that require regeneration or incineration [19,20]. In some recent studies, leaching of harmful contaminants from the spent materials resulted from a removal process was minimized by subjecting the spent materials to a post-treatment using vitrification and treating with geopolymers [21,22]. The principle of using geopolymeric reaction for immobilizing toxic metals is reusing some waste products (such as fly ash and kaolinite) having pozzolanic properties due to the cage structure of geopolymer [23]. However, geopolymer has not been used to solidify the adsorbents encompassing hazardous organic wastes, so far.

Ceratophyllum demersum L. (Hornwort or Coontail) is a submerged aquatic plant which is widely distributed all over the world [24]. It is a rootless, floating, widely distributed, perennial plant. *Ceratophyllum demersum L.* quickly cultivates in small bodies of still water, muddy, quiescent or very slow-flowing water and channels in moderate to tropical zones [25]. Also, *Ceratophyllum demersum L.* sustain low light intensity, specific turbidity, but not salinity. This plant belongs to the *Ceratophyllaceae* family, reproduces by seed and stem fragmentation and grows in depth from 0.5 to 8.5 m [26]. Natural plants are useful components for the aquatic environment because they afford nutrients and housing for wildlife. But they can block water stream, control the work of water pumps, interpose with recreational activities, accommodate mosquito [27]. Also, natural plants can imbalance the oxygen level in the water environment leading to reduce species richness and fish mortality [26]. *Ceratophyllum demersum L.* has a thin stem, needle-like leaves and smooth highly branched in the upper end (up to 60 cm). The leaves containing large chloroplasts show large mesophyll cells and respiratory cavities [24]. Therefore, *Ceratophyllum demersum L.* can be used as a biofilter for different heavy metals such as Pb, Ni, and Cd [25]. Therefore, it has been chosen in this study as a cheap available adsorbent to investigate the removal of model organic contaminants from aqueous solutions. Phenol has been chosen in this study because it is the most common organic pollutant and intermediates in the oxidation pathway of high molecular weight aromatic hydrocarbons.

This work investigates the feasibility of using Al-Shamplan plant for phenol removal from an aqueous solution at different parameters involving: contact time, initial phenol concentration and initial pH of phenol solution. Moreover, the effect of local ambient temperature on the leach-ability of the trapped phenol from the adsorbent to the environment was investigated. For the first time, the stabilization of phenol was explored by geopolymerization. Finally, the equilibrium isotherm models were studied to understand the behavior and type of the adsorption process.

2. Methodology

2.1. Materials

The adsorbent (*Ceratophyllum demersum L.* or Al-Shamplan plant) used for this study was collected from marshes in the south of Iraq. Then, the plant was washed with tap water several times to remove froths, and then dried in the atmosphere for several days than in an oven at 110°C for 24 h. The adsorbent was prepared as a powder using a coffee blender and then it was stored in a desiccator. Al-Shamplan plant was characterized using several equipment's. Atomic absorption spectrophotometer (Perkin-Elmer 5000, UK) was used to obtain chemical analysis. The Fourier-transform infrared spectroscopy (FTIR) (Shimadzu IRPrestige-21, Japan) was used to identify some important functional groups. The adsorbent spectra were measured at wave number within the range of 400–4,000 cm^{-1}. N$_2$ adsorption-desorption isotherms (HORIBA SA-9600 Series, UK) was used to obtain the surface area according to Brunauer–Emmett–Teller (BET) method. The adsorption–desorption isotherms were obtained using N$_2$ at 77 K and P/P_0 (0–0.3).

Phenol (99 wt.%, BDH chemicals, UK) was used to prepare solutions of different concentrations. The effect of the pH of solution on the adsorption of phenol was studied by changing the solution's pH using HCl (conc. 35%–38%, BDH laboratory, US) and NaOH (NaOH pellets 99.9 wt.%, Sigma-Aldrich, Germany). Kaolin (TurboQuant-powders, Iraq) was used as geopolymer raw materials in this study. Sodium silicate solution (0.22 wt.% Na$_2$O and 30.3 wt.% SiO$_2$, JIYIDA, China) was used to prepare the activator solution.

2.2. Experimental work

2.2.1. Adsorption experiments

All adsorption experiments were performed on a batch scale at a room temperature of 20°C. Initially, the contact time was investigated for an initial phenol concentration of 50 ppm and 0.5 g of Al-Shamplan plant was placed in conical flasks containing 25 mL of solutions. The pH of solutions was initially measured to be 5.5. The flasks were shaken at a speed of 250 rpm and samples were taken at different time intervals, filtrated and analyzed. During studying the contact time, the adsorption process continued until the time when there is no significant change occurred in the remaining phenol concentration, which indicated attaining the equilibrium.

The second set of experiments was conducted by preparing different concentrations of phenol in the range of 50–200 ppm to study the effect of initial phenol concentration and equilibrium isotherms. 0.5 g of Al-Shamplan powder was placed conical flasks containing 25 mL of phenol solution. After identifying the equilibrium time based on the results of studying the contact time, the flasks were shaken for 3 h at 250 rpm. The samples were taken at different time intervals, filtrated and analyzed for the remaining concentration of phenol in the aqueous solution. Phenol concentration was determined by measuring absorbency at a wavelength of 270 nm using UV-Spectrophotometer (Shimadzu UV-160A, Japan).

The amount of phenol adsorbed onto Al-Shamplan plant at equilibrium, (q_e mg/g) and the pollutant removal percentage (%R) were calculated according to Eqs. (1) and (2), respectively.

$$q_{(\text{ph})_e} = \frac{\left(C_{(\text{ph})_o} - C_{(\text{ph})_e}\right)V}{w} \tag{1}$$

$$\%R = \frac{C_{(\text{ph})_o} - C_{(\text{ph})_e}}{C_{(\text{ph})_o}} \times 100 \tag{2}$$

where $C_{(\text{ph})o}$ and $C_{(\text{ph})e}$ are the initial and equilibrium concentrations of phenol (mg/L), V is the volume of solution (L) and w is the adsorbent weight (g).

2.2.2. Effect of temperature on the liberation of phenol

Phenol sublimates at 43.15°C, on the other hand, the ambient temperature in Iraq often reaches about 20°C during spring season and to about 50°C during summer season. Therefore, the effect of temperature on the releasing of phenol from the spent adsorbent to the environment at temperatures close to spring and summer temperatures in Iraq when it is disposed of without further treatment was studied.

A sample of the spent adsorbent (0.5 g), which was previously used to remove phenol with an initial concentration of 200 ppm, was left in the environment at 20°C for 30 d to investigate the effect of spring temperature on the releasing of phenol trapped by the adsorbent. Moreover, a sample of the spent adsorbent (0.5 g) was placed in water (100 mL) and exposed to 50°C (inside an oven) for 2 d. Then, the samples were examined by FTIR to identify the change occurring in the functional groups present on the adsorbent surface.

2.2.3. Solidification of phenol-bearing waste

The feasibility of immobilizing the trapped phenol and minimize its liberating to the environment was investigated using geopolymer. The geopolymer was made based on previous procedures mentioned in the literature [28,29]. The geopolymer raw material was activated using an alkaline solution prepared from a homogenous mixing of 3 mL of NaOH solution (10 M) with 0.5 ml of sodium silicate solution. A solid combination of 0.5 g of phenol-bearing materials and 3 g of kaolin was obtained by manual mixing. Next, the combination was blended with 2.5 mL of the activator for 15 min and then poured into a cast mold.

The curing process of samples was performed at room temperature of 20°C for 21 d. The specimens were not dried at a temperature above 50°C to avoid the sublimation of phenol from the specimens. Another mixture of 25 g local clay/1 L water was prepared to examine the leaching of phenol to the environment. The total dissolved solids (TDS meter, HM Digital ZT-2) and pH of the clay-water mixture were measured. Eventually, the solidified samples and phenol-bearing Al-Shamplan were immersed in water and clay-water mixture at 20°C. The concentration of phenol released to the solution was measured after 1, 7, 14, 21 and 30 d.

3. Results and discussion

3.1. Characterization of adsorbent

The chemical analysis results of Al-Shamplan plant presented in Table 1 show that it contains 50.5% of carbon, then 6.3% of iron, 0.7% of nitrogen, 0.24% of phosphor, 0.33% calcium and the rest is distributed between oxygen and hydrogen. These results indicate that the Al-Shamplan plant is minerals-rich material, provides low surface area and thus low porosity. And this was confirmed by the value of the adsorbent surface area obtained as 3.7 m²/g. Comparing to activated carbon and zeolites, Al-Shamplan plant is low surface area absorbent, however, it offers low-cost separation process and green technology which requires no preparation or purchasing.

The important functional groups affecting the adsorption efficiency was obtained using FTIR and the results are presented in Fig. 1. A number of absorption peaks appear in the FTIR spectra of the fresh adsorbent which refers to the complex nature of the adsorbent. The FTIR spectrum showed a broad absorption peak at 3,417.86; 1,651.07; 1,435.04; 1,415.75; 1,087.85; and 1,014.56 cm^{-1} due to the presence of alcohol (O–H stretch), primary amines (N–H bend), alkanes (C–H bend), aromatics (C=C stretch) aliphatic amines (C–N stretch) and esters (C–O stretch), respectively. The shift occurring in the absorption peaks indicates the presence of a metal-binding process taking place on the surface of the adsorbent. It can be referred to that the presence of functional groups corresponding to carbon is due to the fact that carbon composes 50% of the carbon composition as shown in Table 1.
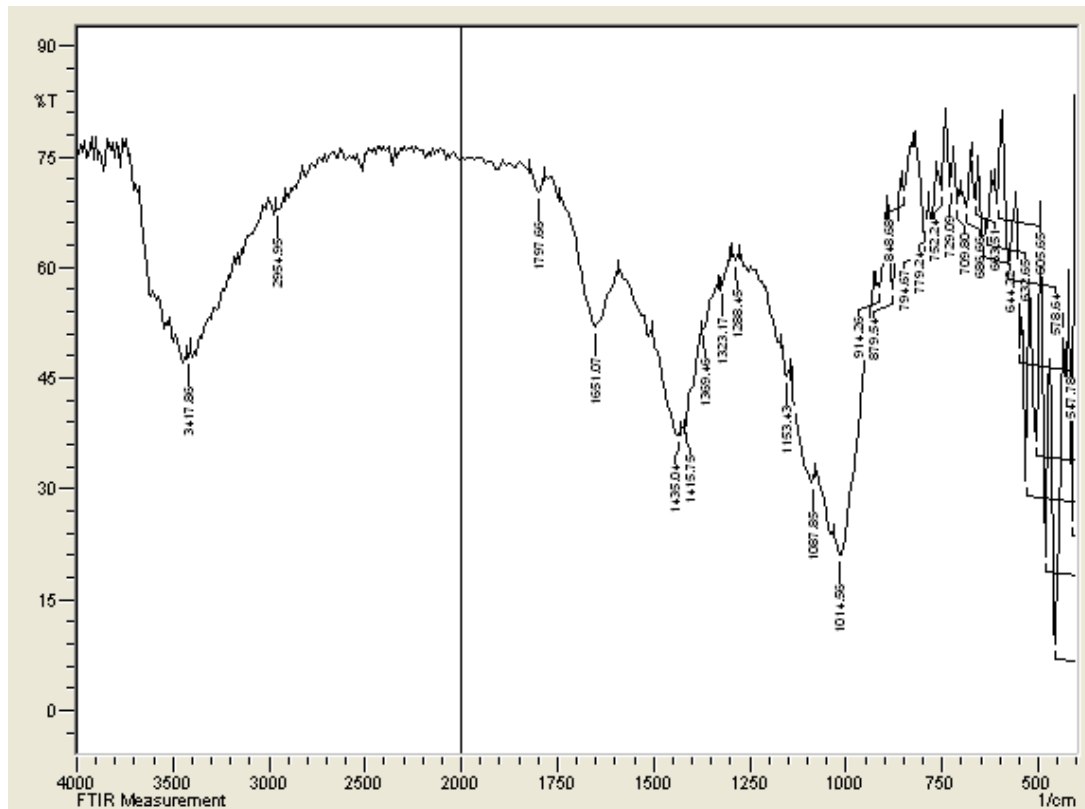
Fig. 1. FTIR of Al-Shamplan plant before being used for adsorption of phenol.

Table 1
Characterization of the adsorbent

	Chemical analysis, wt.%				BET surface area, m²/g
C	Fe	N	P	Ca	
50.5	6.3	0.7	0.24	0.33	3.7

3.2. Adsorption study

3.2.1. Effect of contact time

The results explaining the effect of contact time on the adsorption of phenol by Al-Shamplan are shown in Fig. 2. Adsorption process by Al-Shamplan was conducted for 225 min because it showed that there was no significant change in the phenol remaining concentration for the last three interval times. Fig. 2 shows that the adsorption of phenol rapidly increased and reached equilibrium at about 180 min. Initially, the surface area of Al-Shamplan is vacant of phenol, thus the driving force for adsorption process is large enough for occurring a rapid uptake within the first 50 min. After that, the adsorption process becomes slower due to reducing the concentration difference on the interfacial surface of the adsorbent. Al-Shamplan removed 90% of phenol initially entering the process which can be attributed to the non-polar nature of phenol makes its affinity to be adsorbed higher than its affinity to be binding with water molecules. In comparison, *Acacia tortilis* pod shell removed
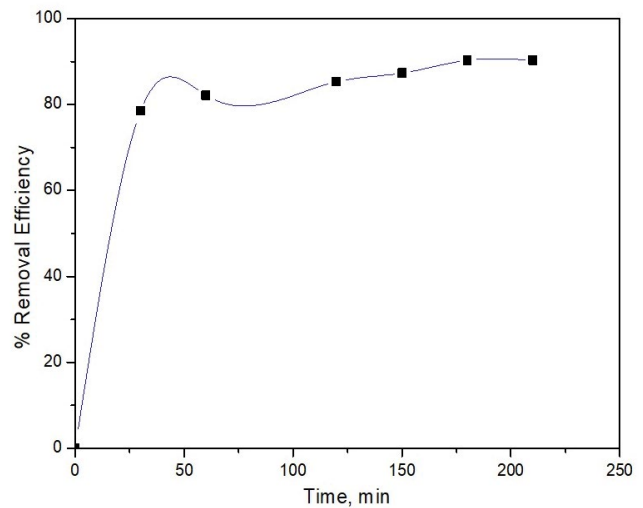

Fig. 2. Effect of contact time on the phenol removal using Al-Shamplan in term of %removal efficiency. Adsorbent dosage of 0.5 g, solution pH of 5.5, mixing speed of 250 rpm, initial phenol concentration of 50 ppm.

95% of phenol when it was used as an adsorbent to remove phenol from an aqueous solution [30].

Fig. 3 presents the FTIR results conducted for a sample of the spent adsorbent. The spent adsorbent showed strong and high-intensity bands corresponding to alcohol
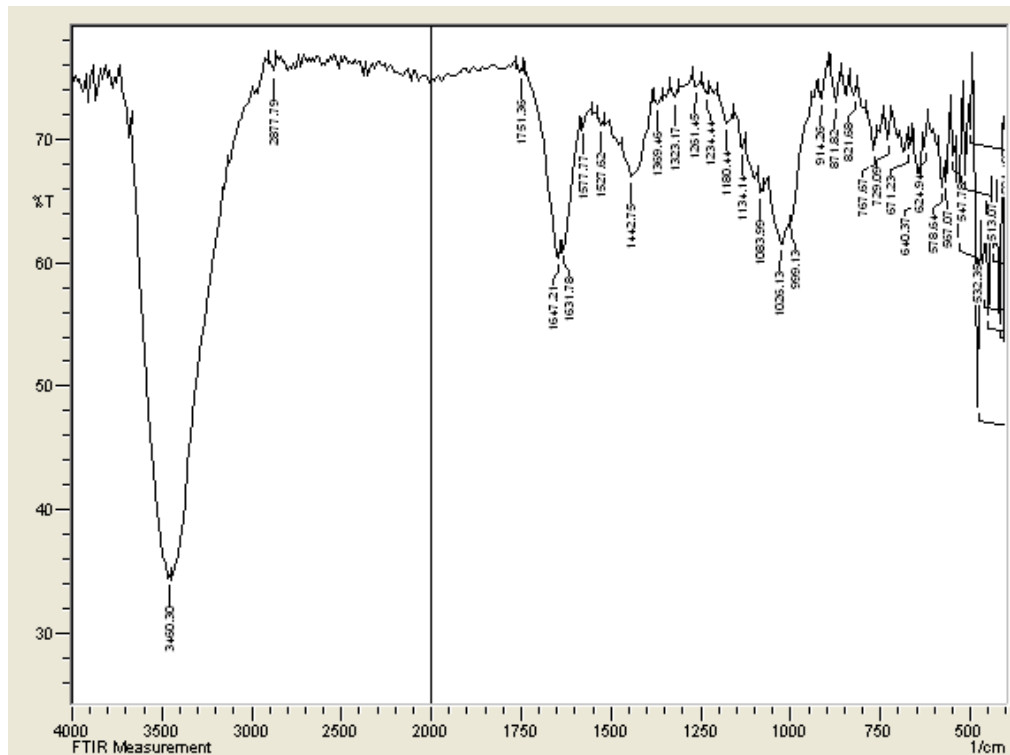
Fig. 3. FTIR of Al-Shamplan plant after being used for 3 h for adsorption of phenol at 20°C.

(O–H stretch) at wave number 3,460.30 cm^{-1}. Generally, the spent adsorbent showed an obvious reduction in the strength of absorption peaks within narrow ranges. Also, new peaks appeared in this sample corresponding to aromatics (C=C stretch) at 1,631.78 and 1,577.77 cm^{-1}, nitro compounds (N–O asymmetric stretch) at 1,527.62 cm^{-1}, aromatics amines (C–N stretch) at 1,261.45 cm^{-1}, methoxy group (asymmetric C–O–C stretch) at 1,234.44 cm^{-1}, alcohol (C–O stretch) at 1,180.44 cm^{-1}, alkyl halides (C–F stretch) at 1,134.14 cm^{-1}, esters (C–O stretch) at 1,026.13 and 999.13 cm^{-1}. The other new peeks appeared after 821.69 cm^{-1} are corresponding to alkyl halides (C–Br stretch), (C–Cl stretch) and (C–I stretch). However, the wave number 1,415.75 cm^{-1}, which was originally present in the fresh adsorbent, disappeared for the spent waste.

3.2.2. Effect of initial pH of the solution

Fig. 4 presents the result of studying the influence of initial pH of phenol solution. A slight increase occurred when pH increased from 3 to 5.5 with a removal efficiency of 93%. Then, the adsorption rapidly dropped when the solution pH decreased. The surface charge and ionization vary with varying pH values. Therefore, the ability to host the adsorbate molecules and the uptake capacity are affected by pH altars. Phenol has (–OH) group of negative charge and its affinity to Al-Shamplan surface increases at acidic medium.

3.2.3. Effect of initial phenol concentrations

The behavior of Al-Shamplan plant for phenol adsorption at different initial phenol concentrations is shown in
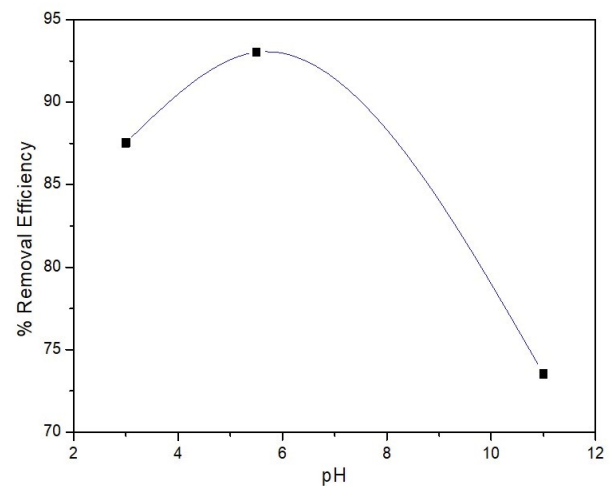

Fig. 4. Effect of initial pH on the phenol removal using Al-Shamplan in term of %Removal Efficiency. Adsorbent dosage of 0.5 g, mixing speed of 250 rpm, initial phenol concentration of 50 ppm.

Fig. 5. The results show that the removal percentage obviously decreased with increasing initial phenol concentration. This behavior can be attributed to using the same surface area provided by the same dose of Al-Shamplan plant used at different concentrations.

3.2.4. Equilibrium isotherms of phenol adsorption

The equilibrium isotherms of the adsorption of phenol using Al-Shamplan plant was studied using Langmuir,
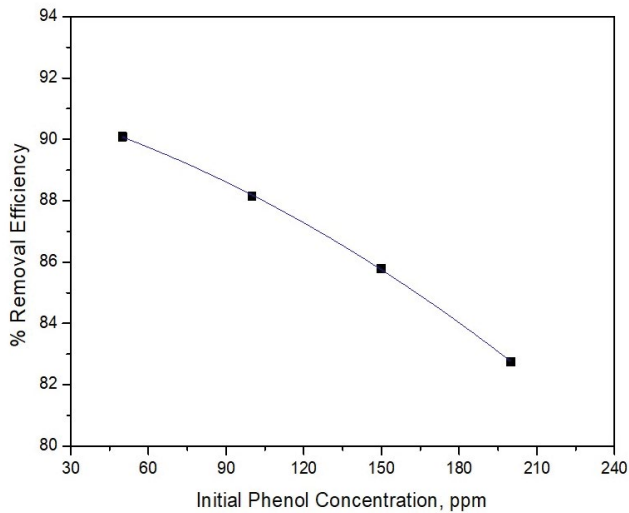
Fig. 5. Effect of initial pH on the phenol removal using Al-Shamplan in term of %removal efficiency. Adsorbent dosage of 0.5 g, mixing speed of 250 rpm, initial phenol concentration of 50 ppm.
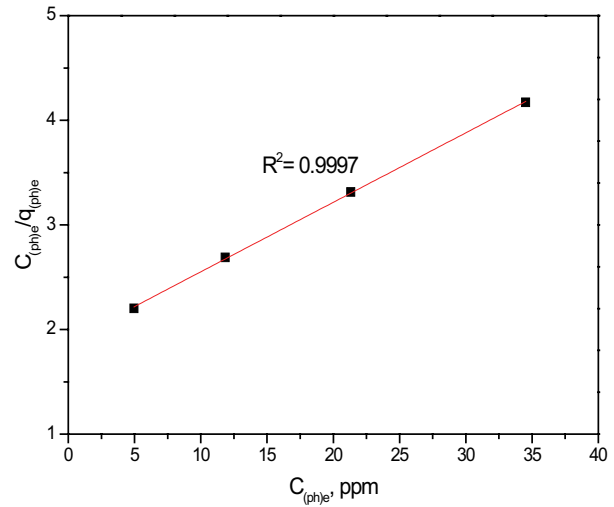

Fig. 6. Langmuir isotherm plot.

Freundlich, and Dubinin–Radushkevich isotherm models. Studying the adsorption isotherms provides useful information about the capacity of biosorbent and its feasibility for wastewater treatment. The adsorption isotherm describes the relation between the adsorbed phenol weight per adsorbent weight at constant initial phenol concentration and temperature [31,32].

The Langmuir model is based on the assumption that the uptake takes place by monolayer sorption on a homogenous surface and no interaction occurs between adsorbates. The linear form of the Langmuir model can be described by Eq. (3) [33,34]:

$$\frac{C_{(ph)_e}}{q_{(ph)_e}} = \frac{1}{bq_m} + \frac{C_{(ph)_e}}{q_m} \tag{3}$$

where $q_{(ph)e}$ is the amount of phenol adsorbed at equilibrium (mg adsorbate/g adsorbent), q_m (mg/g) is the maximum adsorption capacity and b (L/mg) is a Langmuir constant refers to the affinity and energy of adsorption/binding sites. The values of q_m and b can be obtained by plotting $C_{(ph)e}/q_{(ph)e}$ against $C_{(ph)e}$ [35]. The slope of the straight line gives q_m value and intercept of the straight line gives b value as shown in Fig. 6. The values of q_m and b are presented in Table 2.

The Freundlich isotherm model assumes the adsorption occurs on a heterogeneous surface. The linear form of Freundlich isotherm model is given by Eq. (4) [36,37]:

$$\ln q_{(ph)_e} = \ln K_f + \left(\frac{1}{n}\right)\ln C_{(ph)_e} \tag{4}$$

where K_f is a constant indicating the adsorption capacity (mg adsorbate/g adsorbent) and $1/n$ is a constant indicating the intensity of adsorption [35]. For a given sorbate, increasing the value of K_f indicates increasing the adsorption capacity of adsorbent. The $1/n$ magnitude indicates the favorability of adsorption [31]. The adsorption is perfect when $0.5 = 1/n > 0.1$, the adsorbate is easy to adsorb when $0.5 < 1/n = 1$; and the adsorbate is difficult to adsorb when $1/n > 1$ [32,38]. The Freundlich isotherm constants can be calculated from plotting $\ln q_{(ph)e}$ against $\ln C_{(ph)e}$. The slope of the straight line gives $1/n$ value and the intercept of the straight line gives K_f value as shown in Fig. 7. The values of $1/n$ and K_f are presented in Table 2.

The Dubinin–Radushkevich (D–R) isotherm model describes the adsorption process either on homogenous or heterogeneous surfaces and deeply illustrates the adsorption mechanism. The linear form of D–R isotherm can be shown in Eq. (5) [39]:

$$\ln q_{(ph)_e} = \ln q_m + \beta\varepsilon^2 \tag{5}$$

where q_m is the theoretical saturation capacity (mg/g), β is a constant related to the mean free energy of adsorption (mol²/kJ²); and ε is the Polanyi potential which can be expressed in Eq. (6) [40]:

$$\varepsilon = RT\ln\left(1 + \left(1/C_{(ph)_e}\right)\right) \tag{6}$$

Table 2
Constant values for Langmuir, Freundlich and Dubinin–Radushkevich isotherm models for adsorption of phenol using Al-Shamplan

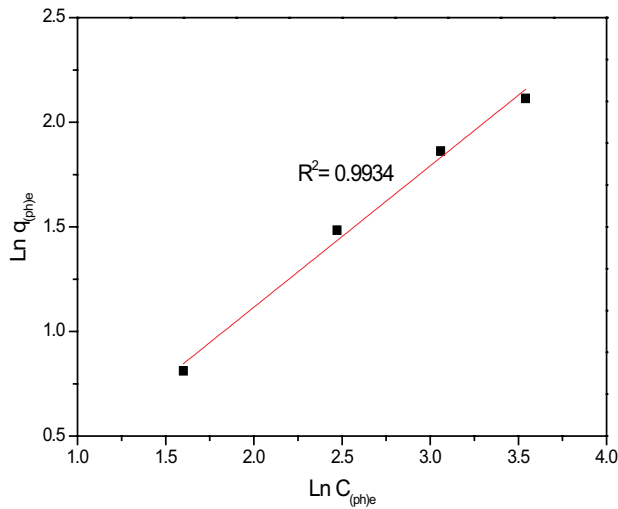| Langmuir isotherm model			Freundlich isotherm model			Dubinin–Radushkevich isotherm model			
q_m, mg/g	B, L/mg	R^2	K_f, mg/g	$1/n$	R^2	q_m, mg/g	β, mol²/kJ²	E, kJ/mol	R^2
15.060	0.035	0.9997	0.790	0.676	0.9934	6.976	6×10^{-6}	0.289	0.9013

Fig. 7. Freundlich isotherm plot.

Fig. 8. Dubinin–Radushkevich isotherm plot.

where R is the gas constant (J/mol.K) and T is the absolute temperature (K). The slope of the straight line gives β value and intercept of the straight line gives q_m value as shown in Fig. 8. The values of β and q_m are presented in Table 2. The mean free energy of adsorption (E) is the energy of transforming one mole of a species from infinity in the solution to the adsorbent surface (kJ/mol) [41,42]; and it can be calculated as shown in Eq. (7):

$$E = \frac{1}{\sqrt{2\beta}} \tag{7}$$

Physical adsorption occurs when E value is in the range of 1–8 kJ/mol. And the adsorption process follows by ion-exchange when E value is in the range of 8–16 kJ/mol. However, the adsorption process is chemisorption when E value is in the range of 20–40 kJ/mol [31,38].

Comparison based on R^2 indicates that the experimental equilibrium data of phenol adsorption using Al-Shamplan are well fitted to the Langmuir model which postulated a monolayer adsorption. Also, the value of $1/n$ was within the range of $0.5 < 1/n = 1$ which indicates the easy adsorption of phenol on Al-Shamplan surface. However, to understand the adsorption mechanism of the process, more information is required as E value obtained was less than 1 kJ/mol. This can indicate the adsorption of phenol is likely physical adsorption dominated by Van der Waals force.

3.3. Effect of temperature on the liberation of phenol

The adsorption results proved the successful utilization of Al-Shamplan plant as an adsorbent to uptake phenol from contaminated water. Samples of the spent adsorbent were examined for liberating the trapped phenol at a local ambient temperature of Iraq in spring and summer. Fig. 9 presents the FTIR results conducted for a sample of the spent adsorbent after 30 d at 20°C. In general, the FTIR of the spent adsorbent after 30 d at 20°C was approximately similar to the FTIR of the fresh adsorbent which can be attributed to liberating of the phenol adsorbed. Both wave numbers 3,417.86 and
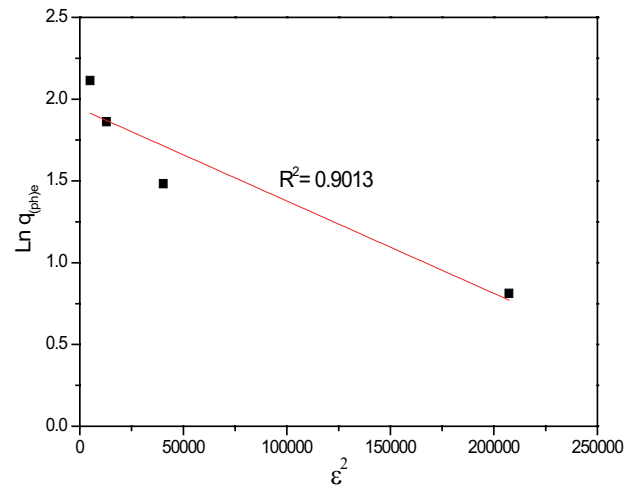
1,014.56 cm⁻¹ which appeared in the fresh adsorbent and corresponding to alcohol (O–H stretch) and esters (C–O stretch), respectively, disappeared for the spent adsorbent left at 20°C for 30 d. The wave number 1,415.75 cm⁻¹ and other several peaks disappeared for the spent waste and after 30 d at 20°C which can be attributed to releasing of other species originally present in Al-Shamplan plant.

Also, the results showed strong and sharp absorption peaks, except a very broadband corresponding to alcohol (O–H stretch) appeared at wave number 3,398.57 cm⁻¹ which can be relative to adsorbed phenol. The strong absorption band observed at 2,962.66 cm⁻¹ due to the stretching vibration of C–H (alkanes), 1,867.09 cm⁻¹ due to the C=O stretching of carboxylic acids and 1,033.85 cm⁻¹ due to the C–N stretching of aliphatic amines. The presence of new bands after around 563.21 cm⁻¹ confirmed the stretching vibration of C–Br denotative of alkyl halides.

Table 3 presents the concentration of phenol released to water at 50°C and the associated TDS. At 50°C, the concentration of released phenol increased from 44.792 ppm after 3 h to 48.750 ppm after 1 d; and very slightly increased to 49.167 ppm after 2 d. These results were confirmed by the almost fixed values of all TDS readings. This can be because adsorption is an exothermic process and increasing the temperature promotes phenol desorption from Al-Shamplan surface. Also, phenol has low sublimation temperature aids the releasing of phenol at temperature reaches 50°C. While at 20°C, the concentration of phenol leached to water was 7.083 ppm after 1 d, but it continuously increased to 9.458 ppm after 30 d as shown in Table 4.

FTIR was conducted for the spent adsorbent after exposure to 50°C for 2 d and the results are shown in Fig. 10. The results showed that three new peaks appeared in this sample corresponding to alkanes (C–H symmetric and asymmetric stretching vibration) at 2,943.37; 2,916.36; and 2,850.79 cm⁻¹. Also, two new peaks appeared at 2,511.32 and 2,380.11 cm⁻¹ corresponds to alcohol (O–H stretch). The new peaks appeared at 1,755.22; 1,647.21; 690.52; 586.36; 516.92; 462.92; and 435.91 cm⁻¹ correspond to carboxylic acid (C=O stretching), aromatics (C=C stretch), aromatics amines (C–N stretch), alkyl halides (C–Br stretch), (C–Cl stretch) and C–O
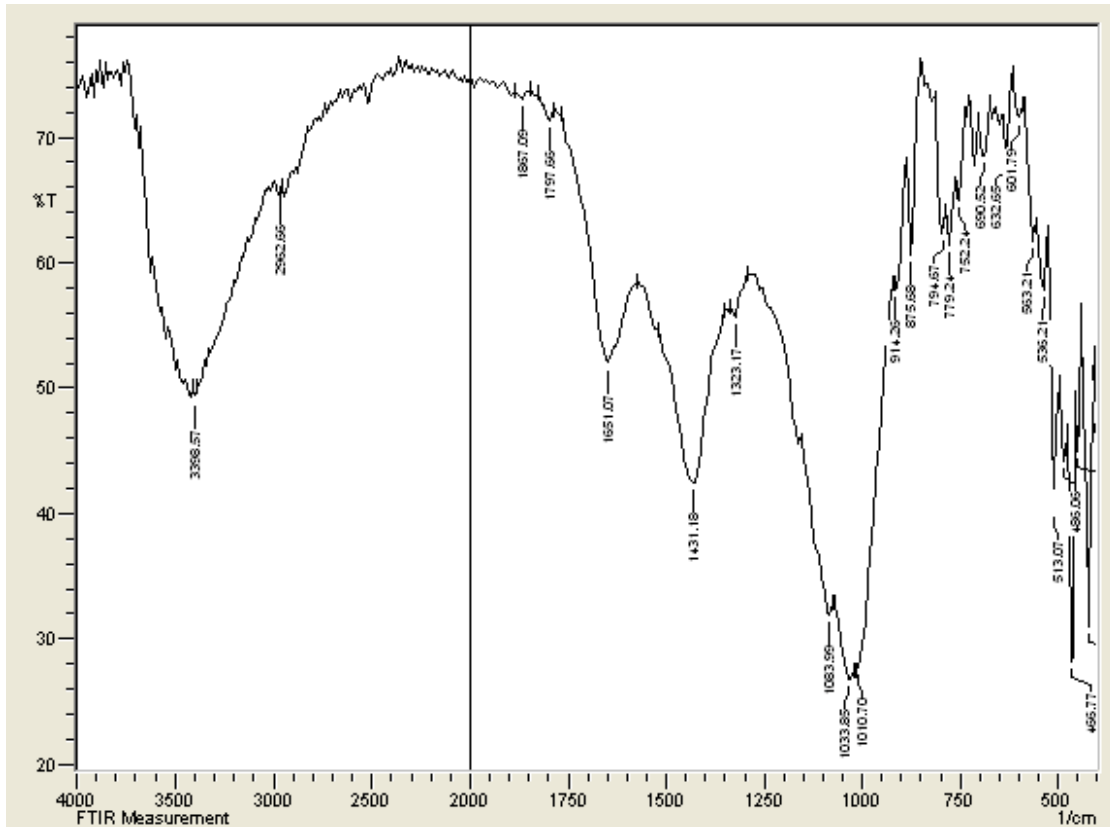
Fig. 9. FTIR of the spent Al-Shamplan plant after being left at the environment temperature (20°C) for 30 d.

Table 3
TDS and Concentration of phenol released to water at 50°C

Contact time, h	Phenol conc. released to water, ppm	TDS, ppm
3	44.792	203
24	48.750	205
48	49.167	206
Initial TDS of water = 58 ppm, Initial pH = 6.8		

Table 4
TDS and concentration of phenol released to water and clay-water mixture from waste adsorbent before and after solidification

| Contact duration, day	Al-Shamplan waste in water		Al-Shamplan waste in clay-water mixture		Solidified Al-Shamplan in water		Solidified Al-Shamplan in clay-water mixture	
	Phenol conc., ppm	TDS, ppm	Phenol conc., ppm	TDS, ppm	Phenol conc., ppm	TDS, ppm	Phenol conc., ppm	TDS, ppm
1	7.083	88	3.363	180	1.875	65	2.500	70
7	8.229	96	4.442	186	3.125	74	3.750	74
14	8.813	101	6.135	197	3.125	74	3.654	75
21	9.479	104	6.750	203	3.125	74	3.654	75
30	9.458	104	6.769	204	3.125	74	3.462	75
Initial TDS of water = 58 ppm, Initial pH = 6.8								
Initial TDS of clay-water mixture = 159 ppm, Initial pH = 6.8								
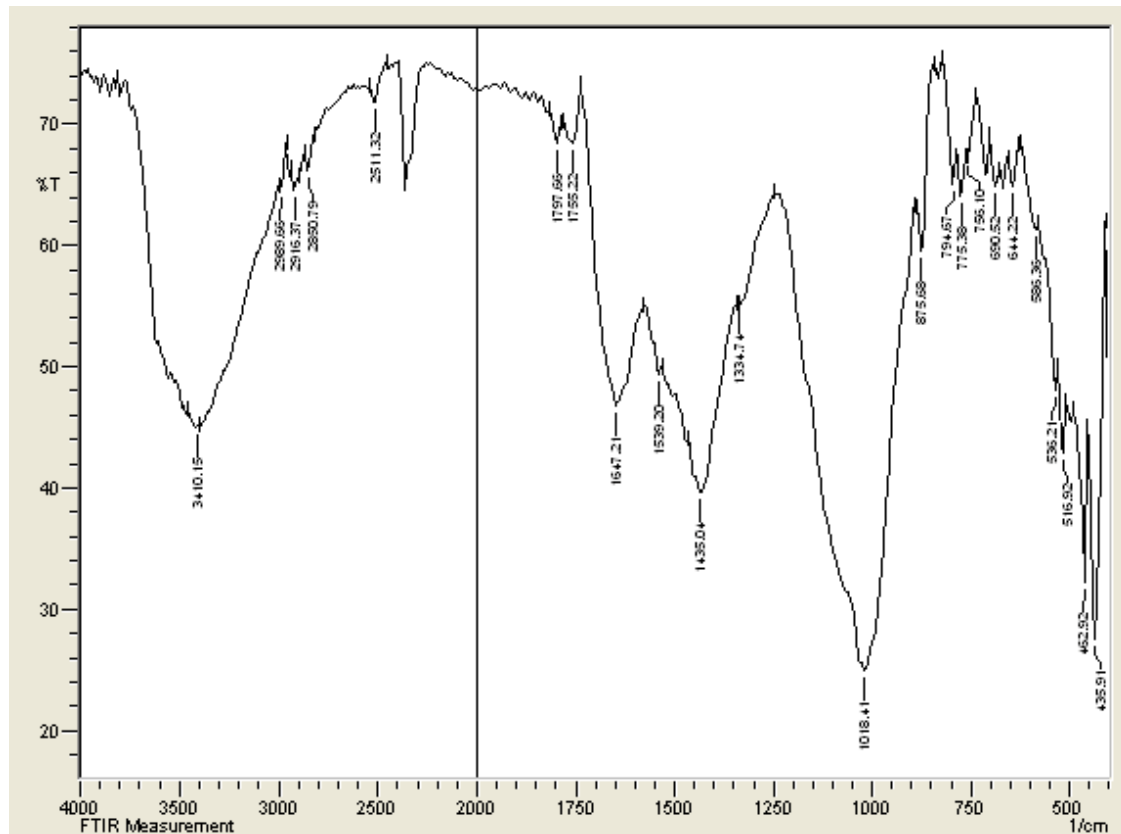
Fig. 10. FTIR of the spent Al-Shamplan plant after being exposed to 50°C for 2 d.

bond. However, the other main peaks appeared in the fresh adsorbent also appeared in this sample with approximately similar intensity.

3.4. Solidification of phenol-bearing waste

The results of solidifying the phenol-bearing adsorbent are shown in Table 4. A comparison between waste samples shows that the concentration of phenol leaching to clay-water mixture at 20°C is less than in case of water. Solidification using geopolymer reduced the leaching rate of phenol with a value of 64.5% after 14 d for the samples placed in water. Also, it reduced with about 40.4% for the samples placed in clay-water mixture. The reduction in the TDS values were 26.7% and 52.8% for the samples placed in water and clay-water mixture, respectively. Another comparison was made relative to the original values of TDS showed that an obvious increase occurred for non-solidified waste. While, the TDS change is higher in case of the waste placed in water. The large driving force due to the concentration difference is the main reason behind these results.

On the other hand, clay contains minerals which simultaneously move to Al-Shamplan surface due to the concentration gradient and this generates a drag force to phenol coming throughout of Al-Shamplan surface. However, the TDS increased for solidified waste placed in water and obviously decreased for solidified waste placed in the clay-water mixture. This can be elucidated as kaolin which was used as a precursor for geopolymer contains alumina which traps the suspended solids as a coagulant agent. Therefore, it can be concluded that solidification the waste adsorbent reduces phenol releasing to the environment and the TDS content as well.

4. Conclusions

Al-Shamplan, an agricultural waste showed a preferable ability for phenol removal through an inexpensive adsorption process. Since the removal efficiency of phenol obtained using Al-Shamplan reached 93% at pH = 5.5. The adsorption of phenol was successfully fitted to the Langmuir isotherm model with R^2 = 0.9997, indicating occurring of the adsorption process on a monolayer. Also, the feasibility of the phenol uptake was confirmed due to that the value of $1/n$ was within the range of $0.5 < 1/n = 1$. The physical adsorption dominated by Van der Waals force likely occurs during phenol removal. The Solidification of the waste adsorbent has coupled actions in the field of treatment of contaminations. This is in terms of trapping the other suspended solid waste causing TDS reduction and minimizing the release of adsorbed phenol to the environment. Since the geopolymerization method significantly reduced the leaching of phenol to 50%.

References

[1]   H. Sassi, G. Lafaye, H. Ben Amor, A. Gannouni, M.R. Jeday, J. Barbier Jr., Wastewater treatment by catalytic wet air oxidation

process over Al-Fe pillared clays synthesized using microwave irradiation, Front. Environ. Sci. Eng., 12 (2018) 1–7.

[2] M. Minière, O. Boutin, A. Soric, Experimental coupling and modelling of wet air oxidation and packed-bed biofilm reactor as an enhanced phenol removal technology, Environ. Sci. Pollut. Res., 24 (2017) 7693–7704.

[3] C. Yu, X. Meng, G. Chen, P. Zhao, Catalytic wet air oxidation of high-concentration organic pollutants by upflow packed-bed reactor using a Ru–Ce catalyst derived from a $Ru_3(CO)_{12}$ precursor, RSC Adv., 6 (2016) 22633–22638.

[4] M. Dinarvand, M. Sohrabi, S.J. Royaee, V. Zeynali, Degradation of phenol by heterogeneous Fenton process in an impinging streams reactor with catalyst bed, Asia-Pac. J. Chem. Eng., 12 (2017) 631–639.

[5] R.R. Zapico, P. Marín, F.V. Díez, S. Ordóñez, Assessment of phenol wet oxidation on CuO/γ-Al_2O_3 catalysts: competition between heterogeneous and leached-copper homogeneous reaction paths, J. Environ. Chem. Eng., 5 (2017) 2570–2578.

[6] Y. Yan, X. Wu, H. Zhang, Catalytic wet peroxide oxidation of phenol over Fe_2O_3/MCM-41 in a fixed bed reactor, Sep. Purif. Technol., 171 (2016) 52–61.

[7] S. Garcia-Segura, L.M. Bellotindos, Y.-H. Huang, E. Brillas, M.-C. Lu, Fluidized-bed Fenton process as alternative waste-water treatment technology-a review, J. Taiwan Inst. Chem. Eng., 67 (2016) 211–225.

[8] M.F. Abid, G.M. Alwan, L.A. Abdul-Ridha, Study on catalytic wet air oxidation process for phenol degradation in synthetic wastewater using trickle bed reactor, Arabian J. Sci. Eng., 41 (2016) 2659–2670.

[9] A. Mani, T. Kulandaivellu, S. Govindaswamy, A.M. Mohan, Fe_3O_4 nanoparticle-encapsulated mesoporous carbon composite: an efficient heterogeneous Fenton catalyst for phenol degradation, Environ. Sci. Pollut. Res., 25 (2018) 20419–20429.

[10] W.T. Mohammed, S.M. Abdullah, A.M. Ghalib, Catalytic wet air oxidation of phenol in a trickle bed reactor, Iraq J. Chem. Pet. Eng., 8 (2007) 45–52.

[11] W.T. Mohammed, S.M. Abdullah, Kinetic study on catalytic wet air oxidation of phenol in a trickle bed, Iraqi J. Chem. Pet. Eng., 9 (2008) 17–23.

[12] C.L. De Silva, R.K. Garlapalli, J.P. Trembly, Removal of phenol from oil/gas produced water using supercritical water treatment with TiO_2 supported MnO_2 ctalyst, J. Environ. Chem. Eng., 5 (2017) 488–493.

[13] M. Qasemi, M. Afsharnia, A. Zarei, A.A. Najfpoor, S. Salari, M. Shams, Phenol removal from aqueous solution using *Citrullus colocynthis* waste ash, Data Br., 18 (2018) 620–628.

[14] H.-M. Zhang, X. Xu, Z. Fan, X. Liu, Z.-C. Wu, M.-H. Zhou, Simultaneous removal of phenol and dichromate from aqueous solution through a phenol-Cr(VI) coupled redox fuel cell reactor, Sep. Purif. Technol., 172 (2017) 152–157.

[15] L.F. Liotta, M. Gruttadauria, G. Di Carlo, G. Perrini, V. Librando, Heterogeneous catalytic degradation of phenolic substrates: catalysts activity, J. Hazard. Mater., 162 (2009) 588–606.

[16] S.M. Al-jubouri, H.A. Sabbar, H.A. Lafta, B.I. Waisi, Effect of synthesis parameters on the formation 4A zeolite crystals: characterization analysis and heavy metals uptake performance study for water treatment, Desal. Water Treat., 165 (2019) 290–300.

[17] S. Petkovic, B. Adnadjevic, J. Jovanovic, Novel kinetics model for adsorption of pollutant from wastewaters onto zeolites. Kinetics of phenol adsorption on zeolite-type silicalite, Adsorpt. Sci. Technol., 37 (2019) 349–364.

[18] E. Bazrafshan, F.K. Mostafapour, H.J. Mansourian, Phenolic compounds: health effects and its removal from aqueous environments by low cost adsorbents, Health Scope, 2 (2013) 65–66.

[19] I. Benhamed, L. Barthe, R. Kessas, C. Julcour, H. Delmas, Effect of transition metal impregnation on oxidative regeneration of activated carbon by catalytic wet air oxidation, Appl. Catal., B, 187 (2016) 228–237.

[20] I. Benhamed, L. Barthe, R. Kessas, H. Delmas, Improvement of (transition metal-modified) activated carbon regeneration by

H_2O_2-promoted catalytic wet air oxidation, Environ. Technol., 39 (2018) 2761–2770.

[21] S.M. Al-Jubouri, N.A. Curry, S.M. Holmes, Hierarchical porous structured zeolite composite for removal of ionic contaminants from waste streams and effective encapsulation of hazardous waste, J. Hazard. Mater., 320 (2016) 241–251.

[22] S.M. Al-Jubouri, S.M. Holmes, Hierarchically porous zeolite X composites for manganese ion-exchange and solidification: equilibrium isotherms, kinetic and thermodynamic studies, Chem. Eng. J., 308 (2017) 476–491.

[23] H. Wang, H. Li, F. Yan, Synthesis and mechanical properties of metakaolinite-based geopolymer, Colloids Surf., A, 268 (2005) 1–6.

[24] G. Borisova, N. Chukina, M. Maleva, M.N.V. Prasad, *Ceratophyllum demersum L.* and *Potamogeton alpinus* Balb. from Iset' River, Ural region, Russia differ in adaptive strategies to heavy metals exposure-a comparative study, Int. J. Phytorem., 16 (2014) 621–633.

[25] M. Chorom, A. Parnian, N. Jaafarzadeh, Nickel removal by the aquatic plant (*Ceratophyllum Demersum L.*), Int. J. Environ. Sci. Dev., 3 (2012) 372–375.

[26] N. Garlich, C. Cruz, A.F. Silva, I.C. Malaspina, R.G. Ferreira, M.G. Tedesque, R.A. Pitelli, S. Bianco, Effectiveness of diquat, copper hydroxide, copper oxychloride and their association in control of submerged macrophytes *Ceratophyllum demersum*, Planta Daninha, 34 (2016) 117–123.

[27] J.M. Di Tomaso, G.B. Kyser, S.R. Oneto, R.G. Wilson, S.B. Orloff, L.W. Anderson, S.D. Wright, J.A. Roncoroni, T.L. Miller, T.S. Prather, C. Ransom, Weed Control in Natural Areas in the Western United States, California, 2013.

[28] A.M.M. Al Bakri, M.T.M. Faheem, A.V. Sandu, A. Alida, M.A.A. Salleh, C.M. Ruzaidi, Microstructure studies on different types of Geopolymer materials, Appl. Mech. Mater., 421 (2013) 384–389.

[29] S. Thokchom, P. Ghosh, S. Ghosh, Effect of water absorption, porosity and sorptivity on durability of geopolymer mortars, ARPN J. Eng. Appl. Sci., 4 (2009) 28–32.

[30] M. Malakootian, A.H. Mahvi, H.J. Mansoorian, N. Khanjani, Agrowaste based ecofriendly bio-adsorbent for the removal of phenol: adsorption and kinetic study by *Acacia tortilis* pod shell, Chiang Mai J. Sci., 45 (2018) 355–368.

[31] M.P. Tavlieva, S.D. Genieva, V.G. Georgieva, L.T. Vlaev, Thermodynamics and kinetics of the removal of manganese(II) ions from aqueous solutions by white rice husk ash, J. Mol. Liq., 211 (2015) 938–947.

[32] H. Tang, W. Zhou, L. Zhang, Adsorption isotherms and kinetics studies of malachite green on chitin hydrogels, J. Hazard. Mater., 209–210 (2012) 218–225.

[33] A. Dehghani, M.H. Zarei, A. Mesdaghinia, R. Nabizadeh, M. Alimohammadi, M. Afsharnia, G. McKay, Production and application of a treated bentonite-chitosan composite for the efficient removal of humic acid from aqueous solution, Chem. Eng. Res. Des., 140 (2018) 102–115.

[34] A.A. Mohammadi, A. Zarei, H. Alidadi, M. Afsharnia, M. Shams, Two-dimensional zeolitic imidazolate framework-8 for efficient removal of phosphate from water, process modeling, optimization, kinetic, and isotherm studies, Desal. Water Treat., 129 (2018) 244–254.

[35] M. Ghaedi, S. Hajati, F. Karimi, B. Barazesh, G. Ghezelbash, Equilibrium, kinetic and isotherm of some metal ion biosorption, J. Ind. Eng. Chem., 19 (2013) 987–992.

[36] M. Qasemi, A. Zarei, M. Afsharnia, R. Salehi, M. Allahdadi, M. Farhang, Data on cadmium removal from synthetic aqueous solution using garbage ash, Data Br., 20 (2018) 1115–1123.

[37] M.H. Dehghani, S. Tajik, A. Panahi, M. Khezri, A. Zarei, Z. Heidarinejad, M. Yousef, Adsorptive removal of noxious cadmium from aqueous solutions using poly urea-formaldehyde: a novel polymer adsorbent, MethodsX., 5 (2018) 1148–1155.

[38] H. Chen, J. Zhao, J. Wu, G. Dai, Isotherm, thermodynamic, kinetics and adsorption mechanism studies of methyl orange by surfactant modified silkworm exuviae, J. Hazard. Mater., 192 (2011) 246–254.

[39] A. Dehghan, A. Zarei, J. Jaafari, M. Shams, A.M. Khaneghah, Tetracycline removal from aqueous solutions using zeolitic imidazolate frameworks with different morphologies: a mathematical modeling, Chemosphere, 217 (2019) 250–260.

[40] S.M. Al-jubouri, S.M. Holmes, Immobilization of cobalt ions using hierarchically porous 4A zeolite-based carbon composites: ion-exchange and solidification, J. Water Process Eng., 33 (2020) 101059.

[41] D. Balarak, F. Mostafapour, H. Azarpira, A. Joghataei, Langmuir, Freundlich, Temkin and Dubinin–radushkevich isotherms studies of equilibrium sorption of Ampicilin unto Montmorillonite nanoparticles, J. Pharm. Res. Int., 20 (2017) 1–9.

[42] S. Puttamat, V. Pavarajarn, Adsorption study for removal of Mn (II) ion in aqueous solution by hydrated ferric (III) oxides, Int. J. Chem. Eng. Appl., 7 (2016) 239–243.