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Removal of Reactive Yellow -145 Dye from Simulated Industrial Waste Waters Over Iraqi Deegle Date Palm Seeds Based Activated Carbons

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Abstract: ***The current study describes synthesis of new type of activated carbon (AC) from Iraqi deegle date palm seeds (IDDPS).This type of AC was synthesizedusing chemical activation method with usingZnCl$_2$ as a chemical activator. The activity of this material as adsorbent was performed via following removal of reactive yellow dye 145 (RYD145) from simulated industrial wastewater. The synthesized AC was investigated using scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) Different physical properties were undertaken such as ash content, adsorption uptake capacity, humidity,point zero charges of the AC were calculated.Removal of this dye was considered to be as a model of the polluted dyes from textile industries and it was treated using batch tests. Removal of this dye in this work was performed applying different reaction parameters and conditions. This including amount of the used AC for each batch, effect of pH on dye removal a, effect of temperature, and duration of time on the adsorption process. The activity of the synthesized AC on dye removal was compared with the non- activated carbon (NAC) that is synthesized from IDDPS. The obtained results showed that AC was more efficient in dye removal in comparison with NAC under the same conditions.***

Keywords: Activated carbons, simulated industrial wastewaters, Iraqi deegleldate palm seeds**,** reactive yellow 145 dye , dyes removal

1. Introduction

In the last few decades high levels of mobility and distributions of industrial dyes in wastewaters have been studied widely by many researchers over all the world. Among many sources of dyes pollution, textile dyeing processes are seemed to be main source for dye pollution as this type of industry use many types of dyes in dyeing units. this type of industries produces industrial wastewaters with high content of dues as well as many of hazard organic compounds. Normally textile industries use many types of natural and synthetic dyes and these dyes have a complex structure. The main problem here is emerged after charging industrial wastewater from dyeing units into the ambient environment close to the textile factories. This industrial wastewaters contains high level of these polluted dyes Generally, wide scales of these dyes are polluted for the environment and can generate carcinogenic and toxic by-products after reaching into the ambient environment such as rivers, soil, and drinking water sources under air conditions as well as interaction with solar radiation[1,2].

Most these dyes have a rigid structure that have a high resistance for decomposition and/or fragmentation under normal conditions of air and sunlight so that these dyes cannot be treated using ordinary physical , chemical and biological treatment methods [3,4]. Generally, the mentioned above methods normallyhave high cost with low removal efficiency, besides that these methods sometimes canproduce sludge and/ or hazard by-products[5,6].Due to these above drawbacks of traditional methods of dye removal from industrial wastewaters, adsorption processes seem to be the most suitable candidate method thatcan exhibit high removal efficiency, relatively low cost , easily processing and reproducibility of the used adsorbent for further usage[7] .

Among different types of adsorbents, activated carbons (ACs) can be a good candidate that can be used with high efficiency and low costly to treat dyes polluted industrial wastewaters[8]. Nowadays, the used commercially available AC is relatively has high cost, this makes its mass applications of in dye removal is not suitable for mass applications. The important point in this context, is how to synthesizeof types of ACs that can be derived from widely available raw materials which can reduce the final cost of the synthetic AC[9]. In this manner, synthesis of AC from agricultural raw materials and /or by products can be an excellent alternative way towards synthesis of low cost with high efficiency of usage and wide applicability for mass applications [10-15].

The present project, involvess synthesis of the AC from Iraqi deegle date palm seeds,this type of ACwas synthesized by physiochemical activation method using ZnCl2 as an chemical activator. The activity of this type of AC was performed by following removal of RY145 by adsorption from the simulated industrial wastewaters..

2. Experimental Part

2.1 Adsorbate

Reactive yellow dye -145 was used in this study as a model of polluted textile dyes), its molecular formula ($C_{28}H_{20}ClN_9Na_4O_{16}S_5$), molecular weight of this dye 1026.26 g/mol, λmax- 416 nm.This dye was provided by Fluka Company 98% and it was used without any further purification.

2.2 Synthesis of the activated carbon (AC)

Iraqi deegle dates palm seeds were used as raw agriculturalmaterials in this work to synthesize this type of AC. Iraqi deegle date palm seeds (IDDPS) were collected from local Iraqi markets, washed with hot distilled water to remove wastes that may present with these seeds. Then these samples were dried at 110 ºC for two hours and mixed with the desired activator in appropriate ratio in a chemical activation process (ZnCl2) for overnight. Then these samples were filtered off and died at 110 ºC for two hours. The dried samples were heated at 700 ºC in a graphite furnace for one hour in under nitrogen flush. Then samples were left to cool to room temperature and the samples were washed again with distilled water. This process was continued until pHs of the washed solutions reach around 7. After that, final products were dried at 110 ºC for two hours to give final activated carbon. Non-activated carbon was synthesized using same IDDPS with following the same method that was used in the synthesis of AC without usinga chemical activator.

2.3 Adsorption Capacity of the Synthesized Activated Carbon

The uptake adsorption capacity of the synthesized AC was conducted by suspension of 0.1 g of AC in aqueous solution of methylene blue (MB), (100 mL, 20 ppm). The mixture was shacked for 24 hours at room temperature under normal air conditions. After that, this mixture was centrifuged carefully to remove particles of the used AC. Theabsorbance of the supernatant liquid was measured at 665 nm using UV-visible spectrophotometer. The adsorption capacity of AC was calculated using a suitable calibration curve of standard solutions of MB to find the amount of the MB dye that was adsorbed on the AC. Then the adsorption uptake capacity of the synthesized AC was calculated by comparing these concentrations with the initial concentration of MB (20 ppm) [16].

2.4 Ash Contents of the Synthesized Activated Carbon

Ash content that is present for the synthesized AC was estimated using a precise weighting of a required amount of carefully dried AC in a finely dried crucible. This then was burned in a furnace at 1000 C for one hourunder normalair conditions. The weight percentage of the ash content for AC was calculated by comparing the remaining amount of material in the crucible was the initial weight of the AC. By comparison this weigh and the initial weight of the taken AC the ash percentage can be calculated [17].

2.5 Humidity of the Synthesized Activated Carbon

Humidity percentage of the AC samples was calculated by subjecting (0.10 g) of dried AC under normal ambient air conditions for overnight. These samples then were weighted accurately, dried in an oven at 110 ºC for one hour. Then the samples reweighed and the percentage of humidity was calculated from differences in the weights for these two cases[18].

2.6 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of surface of AC sample was investigated using FTIR spectroscopy using Perkin Elminer Spectrophotometer. FTIR analysis was recorded in the range of 450 to 4000 cm^{-1}.All FTIR spectra were recorded in range of 450- 4000 cm^{-1} with a resolution power of 1 cm^{-1} for each scan.

2.7 The Point Zero Charge (PZC)

The point zero charges of AC samples were conducted using potentiometric titration method(19) . According to this method, 100 mL of 0.03 M KNO_3 was used as a blank solution.To this solution was added (1mL of 1M) of NaOH, Then the resultantmixture was titrated against nitric acid (0.10M). Asecond mixture of 100 mL of KNO_3 with 0.10 g of the AC was stirred under normal air atmospheric conditions for overnight. To both above final two mixtures, 1.0 mL of NaOH was added and it was titrated with HNO_3 by following the same process that was applied for the blank solution. The obtained titration results were plotted as a volume of the acid against pH of the mixture and the obtained intersection point was taken to be equal to the PZC of the AC. These results are shown in Table 4.

2.8 Scanning Electron Microscopy (SEM)

The surface morphologyof AC was investigated using Scanning Electron Microscope Inspect 550, Netherland (SEM). It was operated at 25 kV. Thestudied AC samples were driedand then were adhesive on carbon tape attached to aluminum – stubbed sputter coated with platinum.

2.9 Adsorption studies

All adsorption studies in this work were performed using a magnetic stirrer at temperatures ranged from 15–30 ºC and all adsorption processes were conducted under normal air conditions. Adsorption processes were carried out using an initial dye concentration of equal to 30 ppm. The used AC was loaded at different massesin a volume of 100 mL of the dye and these masses were as follows: 0.01, 0.05, 0.10, 0.15, 0.20 g. In each experiment, 2 mL of the reaction mixture was withdrawn each ten minutes and for duration of one hour. Then then these samples were centrifuged for several times and the absorbance was followed at a wavelength of 416 nm. The obtained absorbance was recorded using Spectrophotometer Shimadzu 1650 PC-UV-visible. The percentage of dye removal (R%) was calculated using the following relationship [20-22]:

$$R\,\% = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

From above relation, Ci refers to the initial dye concentration (30 ppm), and C_f is the final concentration after one hour of adsorption , and the term q refers to the concentration of the dye that adsorbed on the used AC in (mg/g). The capacity of adsorption at a given time (qt) can be obtained as follows:

$$q_t = \frac{(C_i - C_t)\times v}{m} \qquad (2)$$

According to this relation, C_t is the concentration of the dye as a function of time, the term (v) refers to the volume of solution and (m) is the mass of the used AC.

2.10 Effect of contact time and adsorbent dosage

To study the effects of duration of reaction time and adsorbent masses on dye removal under same applied conditions, a series of experiment were conducted using RY145 (30 ppm, 100 mL). These experiments were performed using different contact times ranged from zero to one hour of reaction time. To investigate effect of mass of the used AC, different masses of AC were used to investigate effect of mass of the adsorbent on dye removal.

2.11 Effect of pH of mixture on dye removal

In order to study the effect of thepHs of the reaction mixture on dye removal from simulated industrial wastewaters a series of experiments were performed. This was achieved by following dye removal under three different pHs values of reaction mixture, these pH values were as follows 3, 7, and 9. The pH of mixture was adjusted to a desired values by genteelly adding of small droplets from 0.1N HCl and NaOH to the initial mixture. The final pH value of reaction mixture was controlled using pH meter measurement .

3. Results and Discussion

3.1 Uptake adsorption capacity of the synthesized activated carbon

Uptake capacity of adsorption for the synthesized AC wascalculated by investigating adsorption of methylene blue dye from the aqueous solution.The obtained results arepresented in Table 1 as (mg/g). These results showed that, the synthesized AC materials in this studyexhibited high external surface areas. This means that these materials have a high porosity in their structures [23,24], and consequently it can beutilized as a good candidate adsorbent materials for many industrial and environmental applications. For a comparison adsorption uptake capacity for non-activated carbon (NAC) was also investigated.

Table 1: Adsorption uptake capacity for the synthesized AC

Sample	AC	NAC
Uptake capacity (mg/g)		

3.2 Ash contents of the synthesized activated carbon

Ash content of the synthesized AC for both activated and non-activated carbon was investigated in this work. It is believed that, ash content for this type of material is due to the existence of non-carbon materials (inorganic materials) within porous structure of AC and NAC. Theseinorganic materials may be found as constituents' materials in the composition of AC. It was found that presence of these residual materials in theporous structure of the synthesized AC can affect negatively on the adsorption capacity of AC. So that presence of these residual materials within structure of AC can reduce its total activity as adsorbents. However,according to the obtained results in the current study, the synthesized AC can be considered as good adsorbent material as it has very low ash content[25]. The results of ash contents for both AC and NAC are summarized in Table 2.

Table 2: Ash content percentages for the synthesized AC

Sample of AC	AC NAC
Ash% (mg/)	0.120.28199.4188.4

3.3 Humidity of the Synthesized Activated Carbon

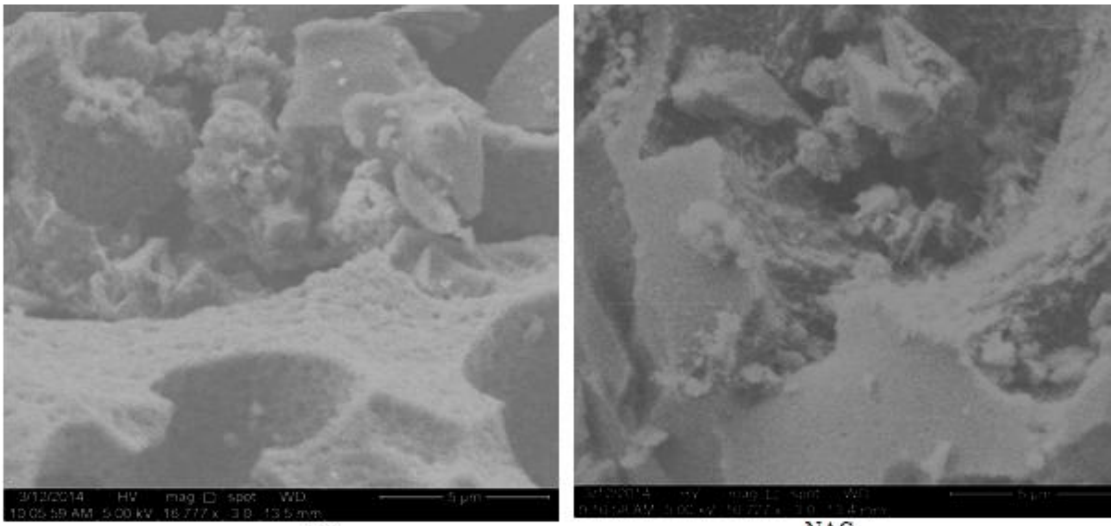
Normally presence of the humidity in AC can be attributed to the ability of AC to adsorb the moister from the ambient environment into the inner porous of the AC. However, from the obtained results in this study it was found high level of moister after subjecting AC into normal air conditions. Also it can be seen that AC has higher value of humidit in comparison with NAC under the same Lab conditions. This probably arise from difference in the porous structure for AC and NACand due to high level of residual inorganic materials that may present within the porous structure of NAC sample[26,27]. These results are presented in Table 3.

Table 3: Percentage of moister content for the synthesized AC

Sample	AC	NAC
Humidity%	4813	

3.4 Scanning electron microscopy (SEM)

Surface morphology of the synthesized AC and NAC was investigated using SEM and the obtained images arepresented in Figure 1. These imagesshowed in general irregular and heterogeneous morphology of the surface for both these two samples.In addition to that, these images showed pores and cavities for carbon samples. It is clear that both of the porosity and cavities are too important for adsorbent surfaces and hence they can improve the efficiency of the adsorbent to uptake dyes and others adsorbents with high efficiency from their solutions. SEM images of these samples are shown in Figure 1.



AC

NAC

Figure 1: SEM images for the AC and NAC samples that synthesized from IDDPS

3.5 FTIR spectroscopies of AC samples

Functional groups of the AC surface were investigated using FTIR spectroscopy. Generally both AC and NAC FTIR spectra are almost similar, these spectra show three main peaks from 1380 to 1690 cm^{-1}.The broad peak that appears around 1690-1715 cm^{-1} can be assigned to the stretching vibration modes for C=O bonds that are present of the both AC and NAC surfaces. The other band thatappeared around 1430 cm^{-1}can be assigned to the stretching vibration mode of C-C bondsof the ACs surfaces[28]. The relatively broad band that appears around 1590 cm^{-1} can beassigned to vibrations modes of aromatic rings that are present on the surface[29]. In addition to that, both of AC and NAC show absorption band around 3000 cm^{-1} which confirms peak confirms the presence of the unsaturated alkynes C=C bond on the AC surface.Thebroad bands that appear around 3300- 3650 cm^{-1}can be assigned to vibration of OH groups[29]. FTIR spectra for AC and NAC samples are presentedin Figure 2.

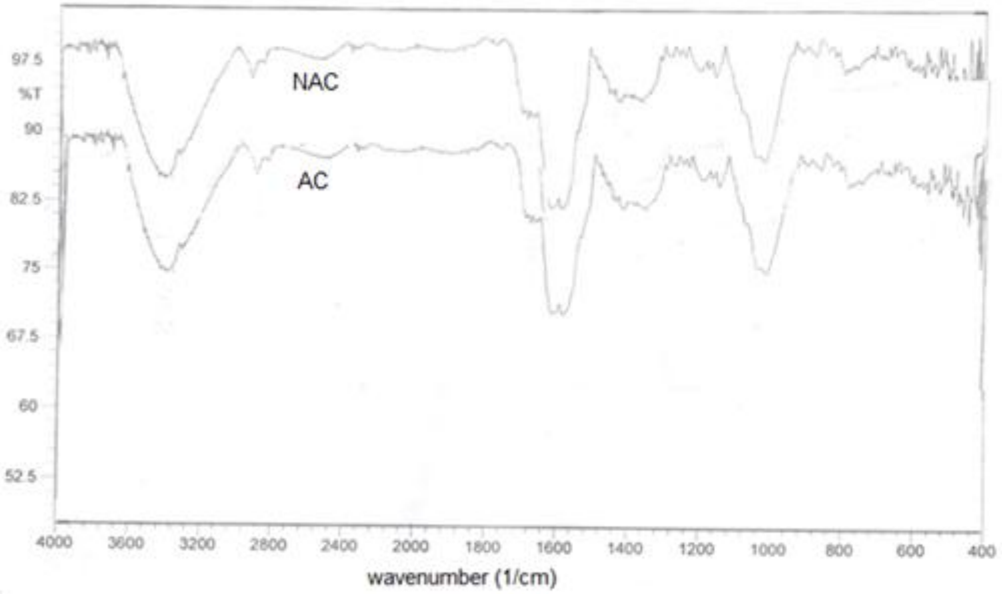


Figure 2: FTIR spectra for AC and NAC samples that synthesized from IDDPS

3.6 The point zero charges of the activated carbon (PZC)

The PZC of the synthesized activated carbon in this study were estimatedusing potentiometric method. The obtained results are shown in Table 5. From these results, the PZCs values of both AC and NAC showed in almost basic value (8.20- 8.45). This indicates that these materials are showed an alkaline pH values. The PZC values of both AC and NAC are presented in Table 4.

Table 4: The point zero charges for the synthesized AC and N AC

Sample	AC	NAC
pH of AC	8.20± 0.1	8.45±0.08

3.7Effect of AC loading and contact time on dye removal

To study the effect of duration of reaction time for the used AC and NAC samples on removal of RY145 from simulated industrial wastewaters. The obtained results for this study are presented in Figure 3. From these results it can be seen that, there is a incrementin the removal of dye upon adsorption on AC and NAC. For all experiment batches, a shaking process for a time duration of one hour at 25 ºC under normal atmospheric conditions was applied to achieve a adsorption equilibration for all doses of the used AC [30]. Generally, the obtained results showed a progress development in dye removal on AC with time for both AC and NAC. This development in dye removal with time for this case is probablydue to increase of uptake adsorption capacities of the used ACs as a function of time.

Comparing the ability of each type of AC in dye removal under the same applied conditions, it can be seen that, AC was more efficient than NAC in dye removal as it shown in Figures3 and 4. This is probably arises from difference in porous structure of AC which makes it has high humidity percentage and low ash contents in comparison with NAC. In addition to that, AC has higher uptake adsorption capacity in comparison with that for NAC. The results of removal of RY145 over both AC and NAC are summarized Figures 3 and 4.

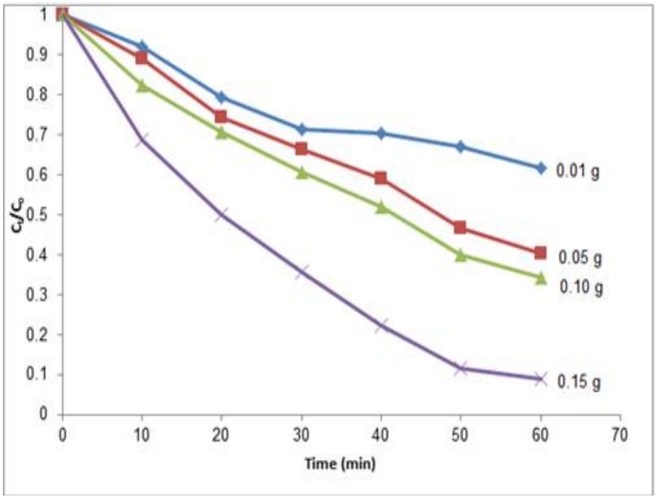


Figure 3: Effect of contact time and dosage of ACon the removal of RY145 dye from simulated wastewaters.

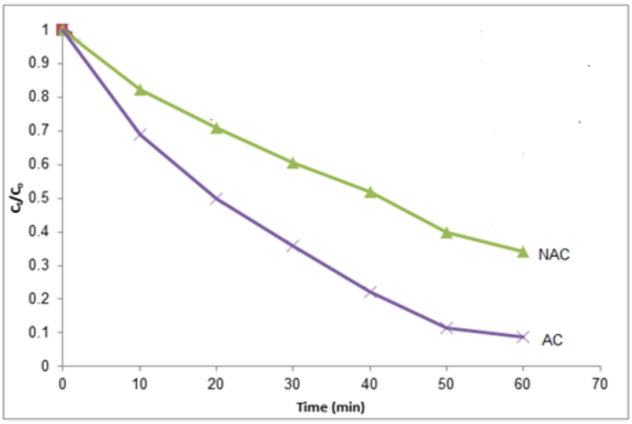


Figure 4: Comparison of activity of AC and NAC on RY145 removal under the same conditions

3.8 Effect of temperature on dye removal over AC

The effect of reaction temperature on dye removal was investigated by performing dye removal over AC at three different temperatures and the obtained results are presented in Figure 5. From these results it can be seen that there was increased in the efficiency of dye removal with increase of the temperature and the best removal was achieved at 30 C and the lowest results was achieved at 20 C.This probably arises from the effect of temperature on increasing of the kinetics energy and this leads to increase the diffusion of the adsorbed species into the surface of the used AC. This process can lead to increase the efficiency of adsorption of RY145 from the bulk into the surface.

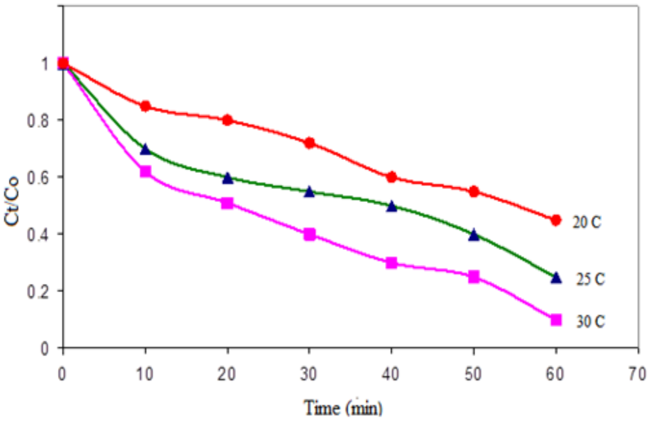


Figure 5: Effect temperature of reaction mixture on adsorption of RY145dye over the used AC

The surface area of the catalyst increases with decreasing of particle size, this can provide more sites that are contributed in the adsorption of the dye. Low efficiency in dye removal at size 100 is probably due to the aggregation of these small particles to form agglomerate in the reaction mixture. This can lead probably to reduce the activity of dye removal using this small particle size[31].

3.9 Effect of pH of reaction mixture on dye removal

pH of reaction mixture can effecton the charge of the surface and this would effect on adsorption/desorption processes on the surface. This depends on the net charge of adsorbed species on the surface. Variation of pH of reaction mixture was conducted by adding controlled amount of acid and base into the reaction mixture and the reaction was performed at three pHs values 3,7, and 9. The results of pH effect on dye removal over AC are summarized in Figure 6.

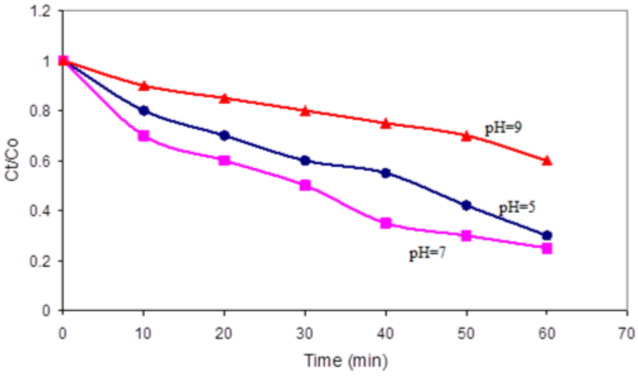


Figure 6: The effect of pH of reaction mixture on the removal of RY145 dye over AC

From these above results,it can be seen that, efficiency ofRY145 dye removal over the used AC were varied with the change in pH values of the reaction mixture and under applying the same reaction conditions. From the obtained results the best removal efficiency for this dye was achieved at neutral media at around pH=7 (around 85%) . On the other hand, the lowest efficiency was obtained at basic media around (pH=9). It is clear that neutral pH value (pH=7) showed higher removal efficiency for the RY145 dye from simulated industrial wastewaters. This observation is probablyarises from low adsorption ability of this dye on the surface at acidic and basic pH values. This probably leads to repulsion between adsorbed species and the surface which reduces the efficiency of dye removal under these conditions [32,33].

4. Conclusions

In this study activated carbon was synthesized from Iraqi deegle date palm seeds using chemical activation method. Adsorption activity of the synthesized AC was investigated by following the removal of RY145 dye from simulated industrial wastewaters. The synthesized ACshowed high uptake adsorption capacity which makes this material as a good candidate adsorbent.In addition to that,this type of AC showed low ash content with high humidity content.

References

[1] G. Walker, L. Hansen, J. Hana, and S. Allen,*Water Res.*,2003, **37**, 2081.
[2] G. Vijayakumarr, R. Tamilarasan, and M. Dharmendirakumar, *J. Mater. Environ. Sci*., 2012, **3(1)**, 157.
[3] M. Stydin, M. Dimitris, and X. Verykios, *Applied Catal. B: Environ*., 2004,**47**, 189.
[4] T. Robinson, G. McMullan, R. Manchant and P. Nigam, *Bioresour. Technol.*, 2001, **77**, 247.
[5] M. Banat, P. Nigam, D. Singh and R. Manchant, *Bioresour. Technol.*, 1996, **58**, 217.
[6] S. Bae and S. Freeman, *Fibers and Polymers*, 2002,**3**, 140.
[7] T. Tsai, Y. Chang, C. Lin, F. Chien, F. Sun and F. Hsieh, *Chemos*., 2001, **45**, 51.
[8] O. Hamdaoui, *J. Hazard Mater*., 2006, **135**, 246.
[9] M. Saquib and M. Muneer, *Dyes and Pigments*, 2003,**56**, 37.
[10] N. Rao, M. Somasekhar, N. Kaul and L. Szpyrkowicz, *J. Chem. Technol.*, 2001,**76**, 1124.
[11] V. Meshko, L. Markovska, M. Miuchera and E. Rodrigues, *Water. Res*., 2001, **35**, 3357.
[12] N. Kannan and M. Sundaram, *Dyes and Pigments*, 2001, **51**, 25.
[13] N. Aukett, N. Quike, S. Riddiford and R. Tennison, *Carbon*, 1992, **30**, 913.
[14] J. Laine, A. Calafta, and M. Labady, *Carbon*, 1989, **27**, 191.
[15] G. Annadurai, S. Juang and J. Lee, *Adv. Environ. Res*., 2002, **6**, 191.
[16] O. Vohler, E. Vonsturn, H. Vonkienel and P. Chmit, Carbon, Ed Vllman's Encyclopedia of Industrial Chemistry, 5th Edition, Berlin, 1986.
[17] Abdullah, A. Kassim, Z. Zainal, M. Hussien, D. Kuang, F. Ahmed and O. Wooi, *Malay. J. Anal. Sci*., 2001, **7**,1.
[18] J. Guo, and A. Luo, *Materials chemistry and physics*, 2003, **80**,114.
[19] J. Vakros, C. Kordulis and A. Lycourghiotis, *Chem. Commun*., 2002, **17**,1980.
[20] F. Hussein, F. Halbus, F. Abdalrazak and Z. Athab.*Journal of Applicable Chemistry*, 2013, **2**, 589.
[21] F. Hussein, A. Halbus and Z. Athab, *Int. J. Chem. Sci.*, 2013, **11**, 3.
[22] A. Kamil, F .Abdalrazak, A. Halbus and F. Hussein,*J. Environ. Anal. Chem*., 2014, **1**, 1.
[23] C. Joseph and A. Kassim, *Borneo Sciences*, 2003, **13**, 71.
[24] J. Luypert, M. Zhang and D. Massart, *Anal. Chimica. Acta*.,2003,**478**, 303.
[25] A.Abdullah, A. kassim, Z. Zainal, M. Hussein, F. Ahmed, and O. Wooi, *Malaysian Journal of Analytical Science*,2001**, 7 (1)**, 65.
[26] Langmuir, *J. Am. Chem. Soc*., 1918, **40**, 1361.
[27] L. Jing, L. Zhong, L. Bing, X. Qibin, and X. Hongxia, *Chinese, J. Chem. Engg.*, 2008, **16**, 871.
[28] H. Freundlich, *J. Phys. Chem*., 1985, **57**, 387.
[29] A. Tor, N. Danaoglu, G. Arslan and Y. Congeloglu, *J. Hazard. Mater.*,2009, **164**, 271.
[30] R. Katal, M. Bae, H. Rahmati and H. Esfandian, *J. Indust. Engg.Chem*., 2012, **18**, 295.
[31] M. Rahman, S. Amin, and A. Alam, Dhaka Uni. J. Sci., 2012, **60(2)**, 185.
[32] K. Ramakrishna and T. Viraraghavan, *Waste Management*, 1997, **8**, 483.
[33] A. Jafar, V. Balakrishnan, S. Arivoli, *Archives of Applied Sci. Res*., 3,145, 2011.