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Reduction of COD in water-based paint wastewater using three types of activated carbon

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ABSTRACT

In this study, the reduction chemical oxygen demand (COD) in water-based paint wastewater using commercial activated carbon, activated date pits and rice husks was investigated. The process was studied in the batch mode with respect to the initial pH, contact time, and adsorbent dose. Adsorption equilibrium and kinetic data were determined for the three adsorbents and were fitted to several isotherm and kinetic models accordingly. The results indicated that activated rice husks (ARH) and activated date pits (ADP) were as effective as commercial activated charcoal (CAC) in the reduction of the effluent COD reaching a maximum of 83% using 180 g/L ARH and 76% using 120 g/L ADP. Kinetically, the results showed that reduction of COD onto both ADP and ARH was better fitted to pseudo-second-order model which involved particle/pore diffusion. In addition, equilibrium adsorption data for the reduction of COD effluent ADP and ARH was best represented by the Langmuir model.

Keywords: COD reduction; Low-cost adsorbents; Water-based paints; Industrial wastewater treatment

1. Introduction

Water-based paints generally consist of organic and inorganic pigments and dyestuffs, extenders, cellulosic and noncellulosic thickeners, latexes, emulsifying agents, antifoaming agents, preservatives, solvents, and coalescing agents [1–6]. About 60–80% of the wastewater generated from the production of water-based paints arise from the cleaning operations of mixers, reactors, blender, packing machines, and floors [1,2,4]. The strength of the generated effluent varies significantly depending on the chemicals used and the type of paint produced. Generally, these wastewaters contain appreciable concentrations of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, highly toxic compounds, and color [1,2,5–8]. Due to the toxic nature and the persistence of its components, effective and economical treatment is required to decrease its pollutant load and remove the associated suspended solids, metal ions, and microorganisms prior to discharge or reuse.

Several methods have been developed for the decontamination of a variety of industrial wastewaters to reduce the associated COD, total organic carbon (TOC), and color [2,5,6,9,10]. However, some of these

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technologies require considerable time, an extensive setup, the addition of chemicals as well as, in the end; some produce large volume of sludge that requires further treatment before disposal. Adsorption techniques have become more popular in recent years in wastewater treatment as they are efficient in the removal of pollutants especially organic pollutants and heavy metals [5,11–14].

Activated carbon has been used to remove COD and BOD from a variety of industrial wastewaters [9,11,12,14–16]. This use of carbonaceous materials for COD reduction has the advantage of producing sludge that is easy to dispose of or reuse compared with conventional precipitation technique [12]. However, one of the disadvantages of applying commercial activated carbon is the high price associated with its production and the difficulty to regenerate it after treatment, which increases the cost of wastewater treatment [14]. This has created a demand for other adsorbents that are inexpensive, efficient and economically viable.

In this effect, low-cost adsorbents, such as some agricultural and industrial wastes, have been studied as viable alternatives to activated carbon for use in wastewater treatment [12–14,17]. However, the choice of adsorbent raw material may be limited to the end use of the activated carbon, availability, cost of the raw material and economic considerations. More specifically, these materials require physical and/or chemical treatment to modify the chemical nature of their surface and enhance their adsorption performance [17,18]. As well, the properties of the finished material are governed not only by the raw material, but also by the method of activation used [19].

Agricultural wastes with appreciable cellulose content show a good potential for the sorption of a variety of wastewater pollutants [20,21]. In Egypt, both rice husks and date pits are problematic agricultural wastes that account for 20% of the rice harvested in tons annually [21,22] and about 10% of the total weight of dates produced [17,23]. Both wastes contain lignin and cellulose which make them amenable for use as inexpensive sorbents for the removal of some organic pollutants [21] and COD reduction in industrial and domestic wastewaters [17,20].

With respect to treatment of water-based paint wastewater, a survey of literature indicated that options commonly used for the decontamination of these effluents involve the application of chemical coagulation [2,24], Fenton reagent [3], and electrochemical/electro-coagulation technique [4,6,8]. However, Kutluay et al. [25] and Malakootian et al. [5] did study the effect of adsorbents such as sodium bentonite and wood ash on the reduction of COD and the removal of Pb and Co in this effluent, respectively. Nonetheless, no report of the application of low-cost adsorbents or commercial activated carbons in the treatment of water-based paint production effluent has been cited in literature. Therefore, in an effort to provide an environmental and economic alternative, the objective of present study is to investigate the effectivity of activated carbon produced from date pits (ADP) and rice husks (ARH) as potential adsorbents for COD in water-based wastewater relative to commercial activated charcoal (CAC). The optimum operating conditions, equilibrium data, and adsorption kinetics for COD removal using the three adsorbent materials were obtained using batch adsorption experiments. The experimental data were fitted to Langmuir and Freundlich models to analyze the adsorption equilibrium.

2. Materials and methods

2.1. *Sorbent materials preparation and characterization*

Date pits (DP) and rice husks (RH) were obtained locally. Before use, both materials were washed thoroughly to remove any dirt and then dried. The process of converting DP and RH into activated carbon was carried out in two stages. First, carbonization of DP and RH was carried out in a muffle furnace at 200–250°C for 2 h. Chemical activation of the carbonized DP and RH was done using 1 M $ZnCl_2$ according to the method described by Yakubu et al. [26]. Each activated material was filtered, washed several times with distilled water until the final solution pH was neutral and then dried in an oven at 100°C for 4 h. Both ADP and ARH were ground using a mortar and were kept in a desiccator for use as is. Commercial acid washed activated carbon (CAC) from RPS Chemical Co., Ltd. (England) was used in the current investigations. The chemical characteristics of the prepared ADP and ARH are provided in Tables 1 and 2, respectively, and the XRD obtained using Bruker AXS-D8 Advance diffractometer for CAC, ADP, and ARH is provided in Fig. 1.

2.2. *Wastewater sampling*

Wastewater samples were collected in clean and washed PE containers from the emulsion paint effluent discharge point before the chemical equalization tank at Pachin Factory for Paints and Chemical Industries, El-Obour City, Egypt. The plant generates around 30 m^3/week effluent with high pollutant load. The effluent is subjected to a chemical treatment prior to being passed through series of baffles to aid in mixing/flocculation before being filtered and discharged

Table 1
Average chemical composition of ADP (% wt/wt)

Characteristic	% wt/wt
Ash content	2.0
Fixed carbon content	67.90
Volatile matter	30.46
Sulfur	1.43
Ash content analysis	
SiO_2	90.56
Fe_2O_3	1.82
CaO	1.09
MgO	1.00
Al_2O_3	0.98
MnO	0.03
K_2O	0.98
TiO_2	0.06
P_2O_5	0.28
ZnO	0.10
Na_2O	0.02

Table 2
Average chemical composition of ARH (% wt/wt)

Characteristic	% wt/wt
Ash content	54.82
Volatile mater	15.62
Carbon content	30.56
Sulfur content	0.32
Volatile content	14.3
Calorific value (kcal/kg)	3,584
Ash content analysis	
SiO_2	88.06
Fe_2O_3	2.86
CaO	3.69
MgO	1.13
Al_2O_3	1.06
MnO	0.04
K_2O	1.86
TiO_2	0.10
P_2O_5	0.25
ZnO	0.13
Na_2O	0.16

to the sewer system. Samples obtained were of the grab-composite type representing a full week of operation including the daily and end-of week cleaning of the production line. Samples were stored at 4°C to avoid any change in their physico-chemical characteristics and were refrigerated during the experimental treatment trials. The basic quality parameters for these wastewater samples were determined according to standard methods [27] and are shown in Table 3.

2.3. COD reduction adsorption experiments

Batch adsorption equilibrium experiments were carried out to determine the optimal conditions for COD reduction in the investigated wastewater using the three types of activated materials. These included the study of the effect of contact time, solution pH, and adsorbent dose. 50 ml of emulsion paint wastewater of a known initial COD concentration were put in 100 ml vessel and were magnetically stirred (speed 800 rpm) with different weights of adsorbent material (1–10 g), at various mixing time (1–200 min) and throughout the pH range of (2–10) at 25 ± 2°C. The treated effluent was then filtered using Whatman filter No. 41 and, during these trials, the COD of both the raw and treated effluent was determined using the closed reflux colorimetric method prescribed by APHA [27]. Effluent COD determinations were carried out in triplicates for each trial, and each trial was repeated 3 times. The COD removal % was calculated as follows:

$$\%\,\text{COD removal} = [C_0 - C_t/C_0] \times 100 \tag{1}$$

and the adsorptive uptake of COD (mg/g) was calculated by

$$q_t = (C_0 - C_t)V/m \tag{2}$$

where C_0 and C_t are the initial and final COD concentration in solution (mg/L), respectively; m is the weight of sorbent used (g) and V is the volume of metal solution (L). At equilibrium contact time t_e, C_t becomes C_e and the amount of COD load sorbed at (q_t) is equivalent to amount at equilibrium (q_e).

3. Results and discussion

3.1. Adsorbent characteristics

Tables 1 and 2 provide the average chemical composition of the prepared ADP and ARH, respectively. It is clear from the data that ARH has a relatively high SiO_2, while ADP has higher carbon content. The XRD (Fig. 1) for ADP indicates a broad spectrum with very few resolved signature peaks corresponding to silicates which are a reflection of its amorphous and low crystalline character. As for ARH, the XRD indicates it was significantly crystalline in nature with signature peaks corresponding to the presence of calcites, silicates and carbon. In the case of CAC, the two

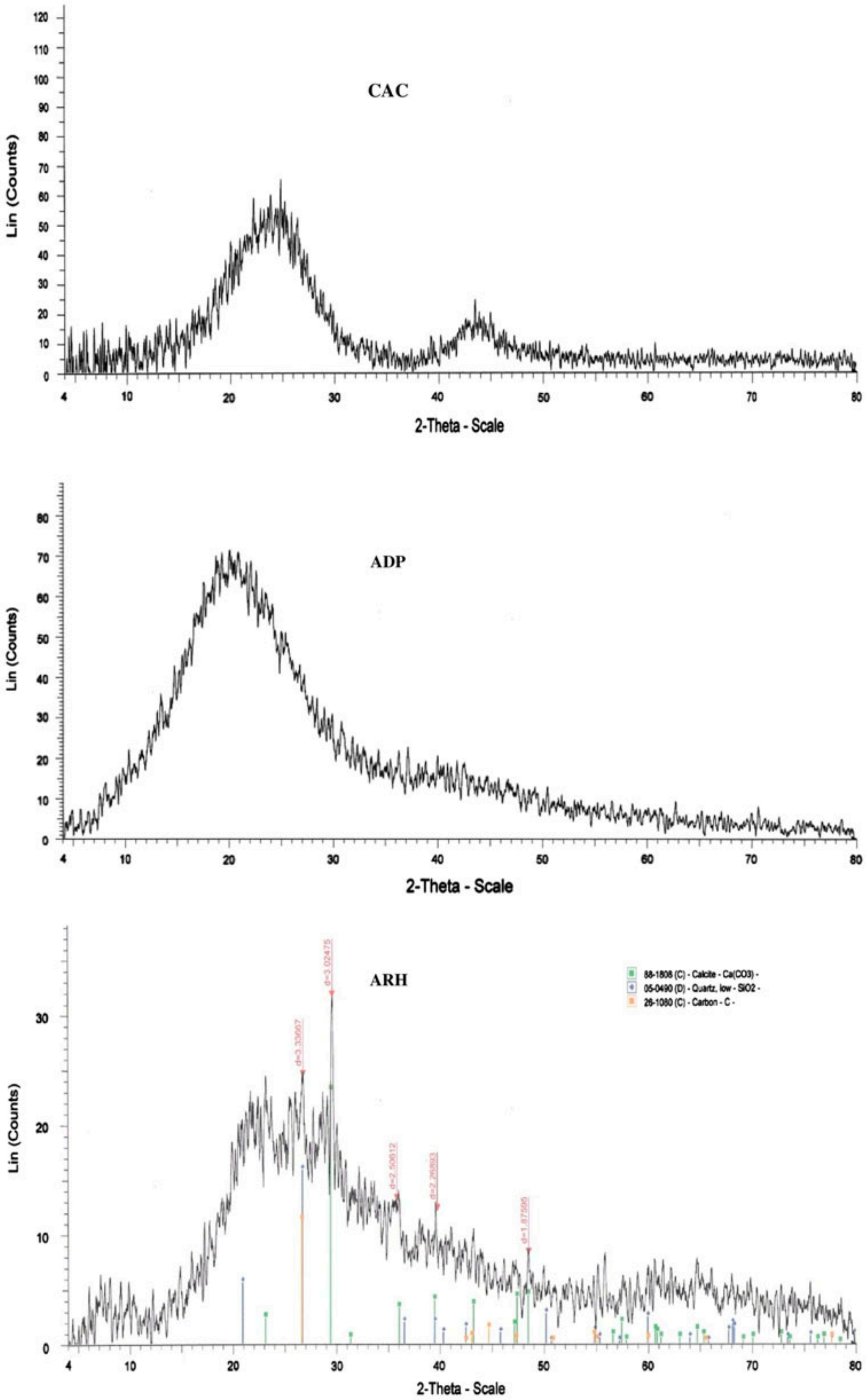

Fig. 1. X-ray diffraction (XRD) spectra of commercial activated carbon (CAC), activated date pits (ADP) and activated rice husks (ARH).

Table 3
Average chemical characteristics of water-based paints discharged effluent

Parameter	Value	Max. allowable (standards decree 44/2000)
pH	5	6–9.5
Temperature	25°C	43°C
COD	6,760 (mg/L)	1,100 mg/l
BOD	4,050 (mg/L)	600 mg/l
TSS	1,160 (mg/L)	800 mg/l
Ni	571.9 (μg/L)	0.2 mg/l
Cr	121.5 (μg/L)	0.5 mg/l
Cu	323.2 (μg/L)	1.5 mg/l
Pb	372.7 (μg/L)	1.0 mg/l

broad peaks at 24 and 42° were attributed to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion [11,28]. It was reported that the increase in silica content of an adsorbent material provides for a good granular structure and a high mechanical strength for better entrapment of organic pollutants in large volume [12]. On the other hand, the increase in carbon content of an adsorbent was reported to significantly increase its adsorption capacity for the removal of organic impurities from solution [29]. As for the effect of chemical activation using $ZnCl_2$, it was reported that using this method for the activation of RH and DP achieved activated carbons with surface area of 811 m^2/g [30] and close to 1,000 m^2/g [31], respectively, the impact of which may be significant upon the adsorbent uptake capacity of each material. In this study, the surface area of the prepared $ZnCl_2$ activated RH and DP was 533.20 and 888.81 m^2/g, respectively.

3.2. Effect of adsorbent weight, stirring/contact time and pH

Fig. 2 shows the effect of varying the adsorbent dose of CAC, ADP, and ARH upon the COD reduction in the investigated wastewater. The results indicate that a maximum COD reduction of 94% was obtained using 100 g/L CAC, 83% using 180 g/L ARH, and 76% using 120 g/L ADP. Therefore, these optimal adsorbent doses were used for the remainder of the experimental trials. These optimal weights reflect the variation in surface area obtained for the prepared activated materials that indicated ADP had a relatively larger surface area than ARH. Previous studies have shown that the application of CAC to wastewaters was effective in achieving over 90% removal of the nonbiodegradable and biodegradable content in wastewater [11,13,29,32–34]. As well, the variation in the observed adsorption capacities among the three adsorbent materials may be attributed to the difference in number of carbonaceous adsorption sites within each [13]. In addition, it may be attributed to the variation of silica content within each adsorbent material which may provide for the better entrapment of pollutants [12]. However, it was observed that in the case of ADP, increasing the adsorbent weight above the optimal dose decreased the COD removal thereafter. This observation is accordance with the findings of El-Naas et al. [17] in their study for the reduction of COD in a petroleum refinery effluent using ADP. This was attributed to the availability of solute, interference between binding sites, electrostatic interactions, and reduced mixing due to the high adsorbent concentration in solution, which in turn decreased the pollutant uptake and the adsorption efficiency.

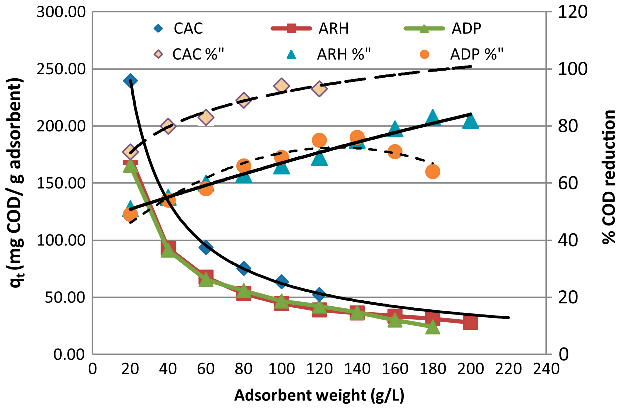

Fig. 2. The effect of adsorbent weight (ADP, ARH and CAC) upon % COD reduction and q_t (mg COD/g adsorbent) at pH 7; $t_{\mathrm{CAC}} = 120$ min, $t_{\mathrm{ADp}} = 120$ min and $t_{\mathrm{ARH}} = 120$ min; $T = 25$°C, volume of solution 50 mL, and $\mathrm{COD_o} = 6{,}760$ mg/L.

The effect of stirring/contact time upon the % COD reduction using fixed optimal adsorbent dose of CAC, ARH and ADP is shown in Fig. 3. The results indicate that both CAC and ARH achieved higher rate of COD removal during the initial 30 min relative to ADP. However, the maximum COD removal attained using ARH and ADP after 120 min was 94 and 84%, respectively, while CAC achieved a 99% COD reduction after 150 min. The times obtained are similar to equilibrium times reported for the reduction of effluent COD via the application of CAC to domestic wastewaters [29] and in acrylic acid wastewaters [34], for using ADP in sugar industry effluent treatment [12] and applying ARH for dye removal from some effluents [10,35].

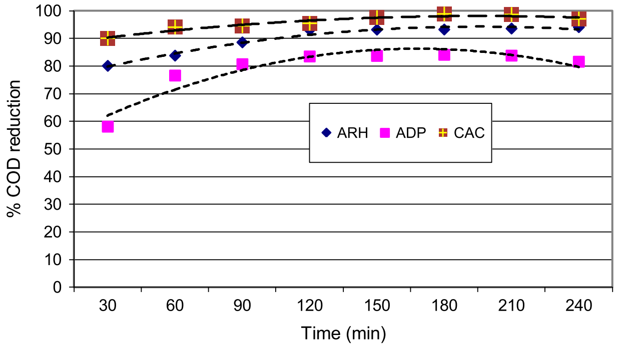

Fig. 3. The effect of varying the stirring/ contact time (min) upon % COD reduction at pH 7, adsorbent weights (100 g/L CAC, 180 g/L ARH and 120 g/L ADP), $T = 25^\circ$C, volume of solution 50 mL, and $COD_o = 6,760$ mg/L.

Faster initial adsorption rates were attributed to the solute being adsorbed onto the surface of the adsorbent particles until surface saturation was reached [16]. After this point, molecules require more time to diffuse through the pores to reach the interior surface of the particles. According to the obtained data, the effect of the formation of a monolayer adsorption and surface mass transfer was more evident in the case of ADP, whereas the linearity of the curves obtained thereafter may be a reflection of intraparticle diffusion at later stage of the process as postulated by Ahmad and Hameed [16] and El-Naas et al. [17].

The pH of the aqueous solution was recognized as one of the most important factors influencing any adsorption process. The effect of pH on COD reduction in water-based paint wastewater was evaluated through the pH range of 2–12 using CAC, ADP, and ARH and the results are depicted in Fig. 4. Overall, no significant variation in the equilibrium adsorbent capacity of CAC, ADP, and ARH was observed over the studied pH range. In conclusion, pH 7 was used as the optimum pH during further experimental work.

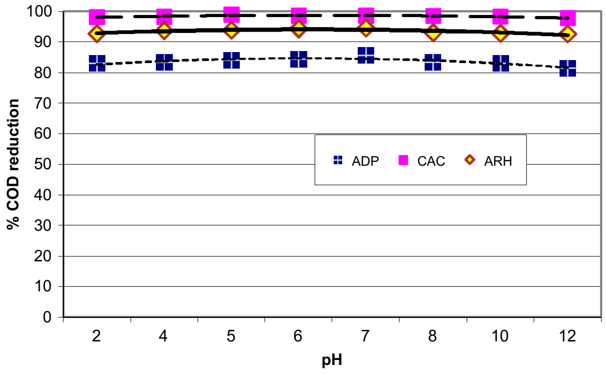

Fig. 4. The effect of varying pH upon % COD reduction, adsorbent weights (100 g/L AC, 180 g/L ARH and 120 g/L ADP), time = 120 min, $T = 25^\circ$C, volume of solution 50 mL, and $COD_o = 6,760$ mg/L.

Table 4 provides a summary of the main effluent parameters before and after the treatment at optimal conditions. Hierarchal clustering of the measured effluent variables after treatment using the three adsorbent materials was done using "StatistiXL 1.8" incorporated within the Microsoft Excel 2007 (Microsoft® Windows 2007) software program. The result is depicted in the dendogram (Fig. 5) which indicates the splitting of these variables into nine clusters grouped and into two main groups. Group I showed a dependency of metal ion reduction (Ni upon Pb) and (Cu on Cr) upon the solution pH as well as on the adsorbent weight and contact time. Overall, the reduction in final effluent TSS had a significant impact upon the reduction of the variables in Group I. Furthermore, the figure indicates a strong dependence of the reduction in the effluent COD and BOD (Group II) on each other as well as they were distantly associated with the reduction achieved of the other measured parameters/ variables in group I.

3.3. Adsorption isotherms

Adsorption isotherms describe how the adsorbate interacts with the adsorbent and the relationship between the amount adsorbed by a unit weight of solid sorbent and the amount of solute remaining in the solution at equilibrium [36–39]. The Freundlich and Langmuir isotherm equations have been extensively to represent the equilibrium adsorption data obtained from activated carbon-organic contaminant systems [32]. Freundlich isotherm model is based upon the assumption that sorption occurs on heterogeneous surfaces and K_f is useful for the evaluation of the adsorption capacity of solute in dilute solutions [32,40]. The model also assumes that as the adsorbate concentration increases the concentration of adsorbate on adsorbent surface also increases and correspondingly, the sorption energy decreases upon the completion of the sorption centers of the adsorbent [36]. The linear equation for Freundlich isotherm applied was [19,32,35,41]:

$$\ln q_e = \ln K_f + 1/n \ln C_e \qquad (3)$$

where K_f is correlated with the quantity of sorbate associated with the sorbent, and n is the Freundlich isotherm constant related to the strength of the sorption. Table 5 provides the K_f and (n) values obtained for CAC, ADP, and ARH removal of COD in the

Table 4
Main mean parameters of water-based paints discharged effluent before and after treatment with CAC, ARH and ADP (optimum conditions) relative to Egyptian standards and current chemical coagulation treatment system

Parameter	Raw WW	AC	ADP	ARH	Max. allowable (standards decree 44/2000)	Effluent after current coagulation treatment[a]
pH	5	7	7	7	6–9.5	7.8
COD (mg/L)	6,760	81	1,080	412	1,100	801
BOD (mg/L)	4,050	70	250	120	600	385
TSS (mg/L)	1,160	696	756	720	800	229
Cr (mg/L)	0.122	0.110	0.101	0.106	0.2	0.002
Cu (mg/L)	0.324	0.049	0.220	0.080	0.5	0.002
Ni (mg/L)	0.373	0.330	0.309	0.362	1.5	0.001
Pb (mg/L)	0.572	0.192	0.471	0.183	1.0	0.015

[a] The current treatment processes 30 m^3/day during the morning 8 h shift.

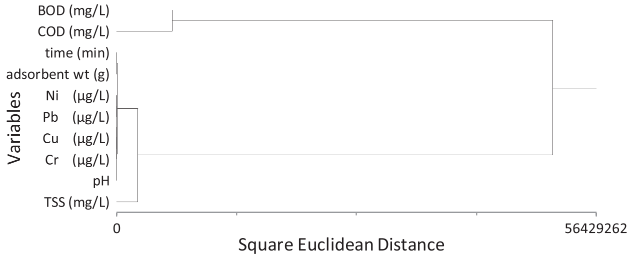

Fig. 5. Dendogram depicts the relationship between reduced treated effluent main parameters and the optimum adsorbent dose (CAC, ARH, and ADP), contact time, and solution pH using Ward's methods for minimum variance.

studied paint wastewater. The Freundlich constants (K_f and n) relate to the sorption capacity and sorption intensity of the sorbent (also known as the heterogeneity factor), respectively [10]. These constants also determine the adsorption capacity of organic pollutants and the extent of COD reduction by adsorbents [13]. The larger the value of K_f and the smaller the value of $1/n$, the more effective the adsorbent is for adsorption and the higher the adsorption capacity and, in this case, the easy uptake of COD from wastewater [32,38]. Devi [13] reported that $1/n$ was dependent on the order of reduction in COD concentrations with the adsorbent dose while K_f was dependent upon the extent of COD removal by the adsorbents. A large value of $1/n$ was indicative of a larger change in effectiveness over different equilibrium concentrations [9,18].

Furthermore, values of $1/n$ ranging between ($0 < 1/n < 1$) were considered as a measure of the adsorption intensity or surface heterogeneity, as the system becomes more heterogeneous in nature, the value of $1/n$ gets closer to zero [10,16,32,41]. The magnitude of n, on the other hand, was reported to give an indication of the favorability of adsorption [16,32,41] and the higher the n signifies that the biosorbent surface was heterogeneous in nature and was high enough for effective separation [38]. More specifically, n values ranging between 2–10 represent good, 1–2 moderately difficult and less than 1 denote poor adsorption characteristics of the adsorbent [16,32,41]. Concerning the data obtained in this study, the values obtained for n were less than 1 for both ADP and ARH, which may be indicative that it was less favorable compared with the adsorption on CAC, which was moderately difficult. Moreover, it was reported that a value for $1/n$ below 1 may be indicative of a normal Langmuir isotherm, while $1/n$ above 1 was indicative of cooperative adsorption [19,32]. In the current study, the values obtained for K_f for ADP and ARH were significantly smaller in magnitude than

Table 5
Isotherm constants and values of R^2 for CAC, ADP, and ARH at 25°C and $C_o = 6{,}760$ mg/L

Adsorbent	Freundlich isotherm				Langmuir isotherm			
	$1/n$ (mg/L)	n (L/mg)	K_f (K mg/g)	R^2	Q_o (mg/g)	b (L/mg)	R_L	R^2
CAC	0.637	1.5691	3.64	0.9774	476.19	1.352×10^{-3}	0.0986	0.9815
ADP	1.991	0.5023	3.11×10^{-5}	0.8387	114.94	0.235×10^{-3}	0.3865	0.9228
ARH	1.593	0.6277	1.82×10^{-3}	0.8608	94.34	0.497×10^{-3}	0.2295	0.9606

that obtained for CAC which denotes their ineffectiveness for adsorption according to this model.

The Langmuir model has been successfully applied to explain real adsorption processes for the reduction of COD using adsorbents [16]. The model was used to describe monolayer adsorption of the sorbate based on a kinetic approach and it assumes a uniform surface, single layer of adsorbed material occurring at a constant temperature [18,32,36]. As well, it assumes that these binding sites have the same affinity for adsorption of a single molecular layer and there was no interaction between absorbent molecules [36]. The linear equation of Langmuir isotherm applied was [32,41,42]:

$$1/q_e = 1/(bQ_0C_e) + 1/Q_0 \tag{4}$$

where Q_0 and b are the Langmuir constants related to adsorption capacity and energy of adsorption, respectively. A plot of $1/q_e$ vs. $1/C_e$ resulted in straight lines with a slope of $(1/b\ Q_0)$ and intercept $(1/Q_0)$ (Fig. 6) and the values obtained for the Langmuir constants are shown in Table 5.

The Langmuir constant b reflects quantitatively the affinity between the adsorbent and adsorbate and the higher the value obtained, the higher the affinity for COD adsorption onto the adsorbent material [32]. Moreover, of the essential characteristics of the Langmuir isotherm is the dimensionless constant separation factor for equilibrium parameter, R_L, which is defined as [38,43]:

$$R_L = 1/(1 + bC_0) \tag{5}$$

where b is the Langmuir constant (L/mg) and C_0 (mg/L) is the initial COD concentration. There are four probabilities for the value of R_L: for favorable adsorption $0 < R_L < 1$; for unfavorable adsorption $R_L > 1$; for linear adsorption $R_L = 1$ and for irreversible adsorption $R_L = 0$ [44]. The values for R_L obtained for the studied system (Table 5) indicate favorable adsorption on CAC, ADP, and ARH. In order to assess the suitability of each model for the explanation of the studied process, the calculated correlation coefficient (R^2) for both models were compared and the data indicate that the adsorption data confirms better to the Langmuir model for the three adsorbents rather than to the Freundlich model. As well, it was proposed that for chemisorption process, monolayer coverage of pollutant molecules was the predominant phenomena and, therefore, the adsorption process may be better represented physically by Langmuir isotherm rather than the Freundlich isotherm model [36].

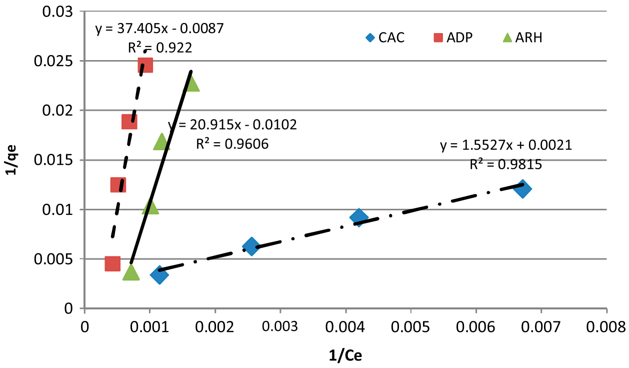

Fig. 6. Langmuir isotherm for COD reduction onto ADP, ARH, and CAC.

3.4. Adsorption kinetics

The COD adsorption rate was determined for CAC, ADP, and ARH by contacting water-based effluent samples with an initial average of 6,760 mg/L with a variable adsorbent dose (20–100 g/L) and at various time intervals. The results are shown in Table 6. The adsorption kinetics may be described as the diffusion through the adsorbent, such as film, pore, and surface diffusions and pore surface adsorption or a combination of these steps [17]. Several kinetic models were tested in order to determine the adsorption controlling mechanism and the minimum time needed to achieve equilibrium. These were the pseudo-first-order and pseudo-second-order equations [17,32] and the intraparticle diffusion [17,19,35].

The linearized form of the Lagergren pseudo-first order model is given as:

$$\ln(q_e - q_t) = \ln(q_e) - k_1t \tag{6}$$

where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t, respectively, and k_1 (min^{-1}) is the kinetic constant for the pseudo-first-order adsorption process. This model assumes that the rate of change of solute uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time [36]. As well, in most cases, this adsorption reaction may be preceded by diffusion through a boundary [36]. The experimental data were fitted to Eq. (6) and the values for k_1 and q_e calculated are provided in Table 6. To quantify the applicability of this model, the correlation coefficient (R^2) was calculated and the results indicated that the correlation coefficients (R^2) for all three adsorbents were far from unity.

The equation used for pseudo-second-order rate is based on the sorption capacity of the solid phase and is given as [45]:

Table 6
Kinetic parameters calculated for the COD reduction /adsorption onto CAC, ARH, and ADP at 25°C, where R^2 is the correlation coefficient

Adsorbent	Dose (g/L)	Pseudo-first-order			Pseudo-second-order			Intra-particle diffusion		
		K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g mg^{-1} min^{-1})	q_e (mg/g)	R^2	K_s (mg g^{-1} $\mathrm{min}^{-0.5}$)	I (mg/g)	R^2
CAC	20	0.0217	318.49	0.9080	0.0340	333.33	0.9919	12.363	254.15	0.9300
	40	0.0219	106.22	0.9148	0.0568	172.41	0.9969	5.4696	131.99	0.9287
	60	0.0217	90.91	0.9091	0.0473	119.05	0.9956	3.5514	88.62	0.9284
	80	0.0219	43.39	0.9084	0.0843	86.96	0.9986	1.6600	73.24	0.9278
	100	0.0217	18.77	0.9097	0.1661	68.49	0.9996	0.7171	62.71	0.9232
ARH	20	0.0290	468.11	0.8542	0.0257	322.58	0.9777	15.214	188.93	0.6841
	60	0.0212	64.18	0.8753	0.0437	108.70	0.9961	4.0536	72.50	0.6857
	100	0.0212	38.51	0.8753	0.0436	65.36	0.9961	2.0679	47.09	0.6860
	140	0.0215	21.31	0.8900	0.0673	46.95	0.9985	1.1143	37.40	0.6951
	180	0.0211	9.94	0.8659	0.1204	36.63	0.9995	0.5893	32.00	0.7301
ADP	20	0.0143	61.56	0.4530	0.0549	238.10	0.9919	9.1714	174.40	0.6835
	60	0.0141	15.88	0.4331	0.0880	83.33	0.9961	2.4229	67.89	0.6674
	100	0.0143	7.41	0.4464	0.1429	75.44	0.9984	1.1029	47.44	0.6689
	140	0.0127	4.47	0.4378	0.2224	40.98	0.9985	0.6514	37.29	0.7132
	180	0.0210	7.91	0.7739	0.0969	29.67	0.9990	0.7000	24.80	0.6744

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{7}$$

where k_2 is the rate constant of second-order adsorption and the slopes of the plots of t/q_t vs. t were used to determine the second order adsorption rate constant k_2. The fitting of the experimental data using the above equation rendered regression coefficient (R^2) near unity (0.99) for the sorption/reduction of COD onto CAC, ARH, and ADP (Fig. 7). As well, the calculated values for q_e were very close to the experimental values. Thus, it may be concluded that the process studied herewith may be better explained by pseudo-second-order kinetic model rather than the first-order model. Furthermore, it was reported that for pseudo-second-order model, the rate-limiting step may be considered to be a surface adsorption process which involves chemisorption mechanism [17,32,36,45]. Thus, in the current study, COD removal from the investigated wastewater may be regarded as a physicochemical interaction between two phases.

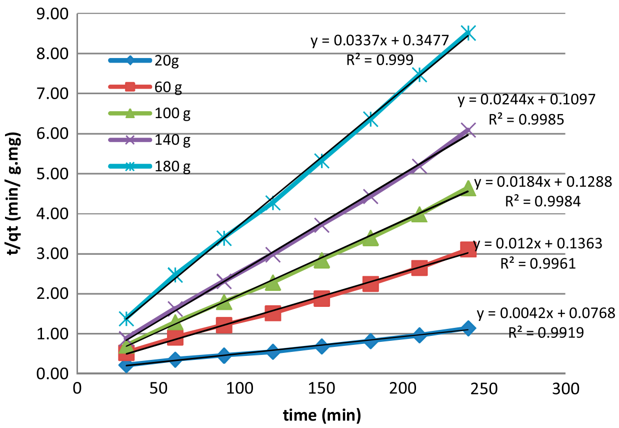

Fig. 7. Second-order kinetics for COD reduction onto ADP.

In many adsorption processes, the adsorbate species may most probably be transported from the bulk of the solution into the solid phase through intraparticle diffusion/transport [10]. For the intraparticle diffusion model, the equation used is given as [10,17,19,35,36,46]:

$$q_t = k_i t^{0.5} + I \tag{8}$$

where q_t is the fraction of pollutant uptake (mg/g) at time t, k_i is the intraparticle-diffusion rate constant ($\mathrm{mg/g\,min^{0.5}}$) and I is the intercept (mg/g). The intercept I represent the effect of the boundary layer thickness and the minimum the intercept values obtained indicates that the adsorption process was less controlled by the boundary layer [36,46]. Furthermore, if the plot of q_t vs. $\sqrt{t}$ passed through the origin, then intraparticle diffusion may be considered as the rate-limiting step [10,19]. Fig. 8 indicates that the obtained plots did not have a zero intercept and were curved to some extent at the initial portion that was followed by a linear portion and a plateau. Similar observations were reported by Bansode et al. [19], Mane et al. [46], Nandi et al. [35], El-Naas et al. [17] and Chowdhury

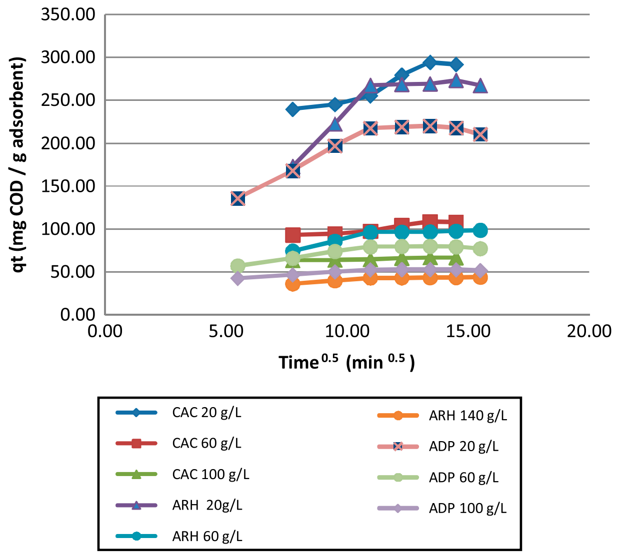

Fig. 8. Intraparticle diffusion model for adsorption/reduction of COD onto CAC, ARH, and ADP. $T = 25^\circ C$, volume of solution 50 mL, and $COD_o = 6{,}760$ mg/L.

et al. [10]. This was taken to be indication that surface adsorption and intraparticle diffusion were concurrently operating during the adsorption process. As well, the noted curvature in the shape of the plot at a small time limit was reported to be due to mass transfer resistance and bulk diffusion, while the linear portion was attributed to intraparticle diffusion [10,46,47]. However, in the case of CAC, it was noted that the R^2 values were between 0.9232 and 0.9300 which may denote that the adsorption process onto CAC tends to proceed as second-order process followed by intraparticle diffusion [10]. On the other hand, as for ARH and ADP, with R^2 not near unity, it may be concluded that particle/pore diffusion was involved, but it was not the only rate limiting mechanism [19,46].

3.5. Environmental and economic considerations

One of the main objectives of this study has been to improve upon the quality of treated wastewater using activated charcoal produced from abundantly available agricultural residues which will in turn decrease the use of chemicals. Another aim was to produce easily filterable sludge that was more amenable for safe disposal or for recycle and reuse. Essentially in the current treatment system, pollutant reduction was carried out by the addition of alum after pH adjustment from 5–6 to between 6.5–9.5 and after effluent disinfection using Cl_2. The process of coagulation/flocculation and gravity settling takes place in the chemical addition tank and the resultant is passed through a filter press after 5 h. For an initial COD of 6,760 mg/L, the solid content in the 30 m^3/day effluent was estimated to be 120 g/L, which is equivalent to 3,600 kg/day.

The chemical analysis of this sludge showed it had the average content of Al_2O_3 (12.42%), TiO_2 (8.37%), SiO_2 (6.37%), CaO (6.15%), S (2.69%), MgO (1.92%), ZnO (0.13%), Fe_2O_3 (0.43%), P_2O_5 (0.08%), V_2O_5 (0.07%), and LOI (58.94%). The noted composition of sludge may be a result of the addition of alum as coagulate/flocculent, which is an observation recorded by Jewell et al. [7]. In the current case, the sludge was either dumped in the desert or together with the municipal solid waste at El-Obour City after being dried using a filter press, which represents an environmental problem.

However, since mid-1990s, some researchers have explored a number of options for the recycling and safe reuse of sludge generated from paint spraying operations [48]. These options included the use of sludge as an additive to Portland cement, the recovery of some of its valuable components through pyrolysis, or its conversion into reusable paint. Recently, Kherzi et al. [49] investigated the option of extracting titanium dioxide from water-based paint sludge and indicated its viability for reuse in paint production, an option which may become economically viable in the future.

Nonetheless, an option of interest has been that explored by Kim et al. [50] since the 1996. This option investigated the recycling and reuse of water-based paint sludge and its applications. They indicated that the charred sludge may be employed in the adsorption of VOCs in scrubber water systems, in canisters for fuel vapor control and as filters for odor control in vehicle components. However, they also reported that enhancing the adsorption properties of this charred sludge was achieved either by mixing it with carbonaceous material such as coal or through the increasing of the carbon black content of the raw paint sludge.

In the current study, the use of adsorbents for COD reduction in this wastewater had the advantage of providing an easily filterable sludge. As well, the use of ARH and ADP increased the carbon content of the obtained sludge as well as made it easily filterable and easily dewatered compared with the current conventional precipitation treatment. This may also decrease the environmental hazards associated with the produced sludge as well as provide more viable alternatives for its reuse [12]. Overall, the technical applicability of activated carbons and cost-effectiveness may be the key factors for the application of adsorbents to treat such an effluent. In general, the only cost incurred in this case was to transport these agricultural residues and for the chemicals used for activation. Moreover, the application of adsorbents within the current treatment system entails a reduction in the use of chemicals as well as a reduction in energy with the decrease in treatment time from 8 h to less than 4 h. Overall, this may increase the prospects for water reuse and sludge recycle options in the near future.

4. Conclusion

During the present study, ADP and ARH were found to be effective adsorbents for the reduction of COD associated with water-based effluent as CAC. The results indicated that a maximum COD reduction of 83% was obtained using 180 g/L ARH and 76% using 120 g/L ADP. The results also showed that reduction of COD onto the ADP and ARH followed second-order rate kinetics which involved particle/pore diffusion, as part of chemisorption controlled mechanism. Equilibrium adsorption data for the reduction of effluent COD using ADP and ARH was best represented by the Langmuir model. Furthermore, the addition/ mixing of adsorbent material to the raw wastewater may produce sludge with a higher carbon content that may significantly increase its potential for reuse and recycle within the industry as well as have some economical consequences in the future.

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