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Reduction of COD in Resin Production Wastewater Using Three Types of Activated Carbon

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Abstract

In this work, the efficiency of activated carbon derived from carbonized date pits (ADP) and rice husks (ARH) was compared with commercial activated carbon (CAC) for the reduction of COD in wastewater arising from resin manufacturing plant. The process was studied in batch mode with employing different absorbents optimizing various parameters, such as adsorbent dosage, contact time and pH. 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 a maximum COD reduction of 92.4% was obtained at pH 2 using 30 g/L CAC, 90.3% using 40g/L ADP and 88.9% using 60 g/L ARH. Kinetically, the results data showed that reduction of COD onto the three adsorbents was better fitted to pseudo second-order model. Equilibrium adsorption data for the reduction of COD effluent using CAC, ADP and ARH were best fitted to the Langmuir isotherm model.

Keywords: COD Reduction, Low Cost Adsorbents, Resin Wastewater Treatment

1 Introduction

Resin is a synthetic polymer and a film-forming component that identifies the paint [1]. The formulation of a paint material and the particular chemicals used are influenced by the particular resin or resin combination used. The blend of resin (sometimes referred to as the binder) and solvent is sometimes referred to as the paint vehicle. Alkyd resins are main product of poly condensation reactions between poly carboxylic acids and poly alcohol present in fatty acids or vegetable oils [2]. These resins are used for decorative painting applications more than other binders because of lower cost; inexpensive raw material, easy manufacturing and high solubility of resin in less expensive solvents.

Several methods have been developed for the decontamination of several industrial wastewaters [3, 4]. These include coagulation, foam flotation, filtration, ion exchange, aerobic and anaerobic treatment, advanced oxidation processes, solvent extraction, adsorption, electrolysis, microbial reduction and activated sludge [4-7].

The content of these wastewaters (also known as process water) arising from resin producing industries is dependent on the manufacturing process as well as the raw materials used and final product. However, these wastewaters are generally characterized by high levels of organic matter and organic nitrogen compounds [8-10]. Thus, biological treatment for the combined carbon and nitrogen removal is required [8, 9]. Nonetheless, after biological treatment, these effluents were found to still contain high concentration of organic nitrogen and dissolved chemical oxygen demand (DCOD) and require further chemical treatment to meet the effluent discharge standard [10].

Activated carbon is considered very effective in reduction of color, absorbable organic halides and non-biodegradable pollutants present in wastewaters [11, 12]. They have been used to remove COD and BOD from many industrial wastewaters [12-16] as well as natural organic matters (NOMs) from raw waters [17]. As well, the combined activated sludge-powdered activated carbon (AS-PAC) system was reported to improve upon biological treatment efficiency, to remove refractory organic compounds, and to enhance nitrification [18]. This was attributed to the PAC enhancing the performance of the system through the biological removal and adsorption of pollutants simultaneously. In addition, it was reported that the biological inhibition caused by some organic compounds decreased due to the presence of PAC. However, of the disadvantages of applying commercial activated carbon is the high price of treatment and difficult regeneration, which increases the cost of wastewater treatment and thus, low cost alternatives have to be investigated in order to overcome this shortcoming [12].

Many researchers have identified a number of low cost adsorbents (agricultural and industrial wastes) as viable alternatives to activated carbon in wastewater treatment [19]. Agricultural materials particularly those containing cellulose shows potential sorption capacity for various pollutants [20]. As well, these materials are subjected to physical and/ or chemical treatment to modify the chemical nature of their surface and to enhance their adsorption performance [19, 21]. However, the selection of the most suitable adsorbent is based upon the end use of the activated carbon, availability, adsorption capacities, cost of the raw

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material and economic considerations [16, 22]. As well, the properties of the finished material are governed not only by the raw material, but also by the method of activation used [22]. In Egypt, rice husks and date pits are problematic agricultural wastes that account for 20% of the rice harvested in tons annually [23, 24] and about 10% of the total weight of dates [19,25]. However, they possess a granular structure as well as being insoluble in water, having a good chemical stability and a high mechanical strength [7]. Overall, both wastes contain lignin and cellulose which make them amenable for use as inexpensive sorbents for the removal of some organic pollutants [23] and COD reduction in wastewaters [19,20].

The purpose of this work is to evaluate the efficiency of activated carbon prepared from carbonized date pits (ADP) and rice husks (ARH) as potential adsorbents for COD reduction in resin wastewater treatment compared 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 hours. Chemical activation of the carbonized DP and RH was done using 1M $ZnCl_2$ 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 hrs. 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 FTIR obtained for CAC, ADP and ARH is provided in Figure 1.

2.2 Wastewater Sampling

The main wastewater streams arising from resin production are resin-water condensation mixture and washing waters from the cleaning of the production reactors [27]. The condensed resin-water mixture is fed to a gravity separator for the removal of liquid resin, which is recycled to the reactor while the resulting water is treated in a special incinerator and used as a fuel. After process completion, the reactors are washed with caustic soda solution (2%) at 90°C and the wastewater is discharged to the current treatment facility. Samples were collected in clean and washed PE containers from the resin effluent discharge point before the aerated equalization balance tank at PACHIN Factory for Paints and Chemical Industries, El-Obour City, Egypt.

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)	3584
Ash content Analysis	%wt /wt
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*

The plant generates around 20 m^3/week effluent with high pollutant load. 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 [28] 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 (CAC, ADP and ARH).

These included the study of the effect of contact time, solution pH, and adsorbent dose.

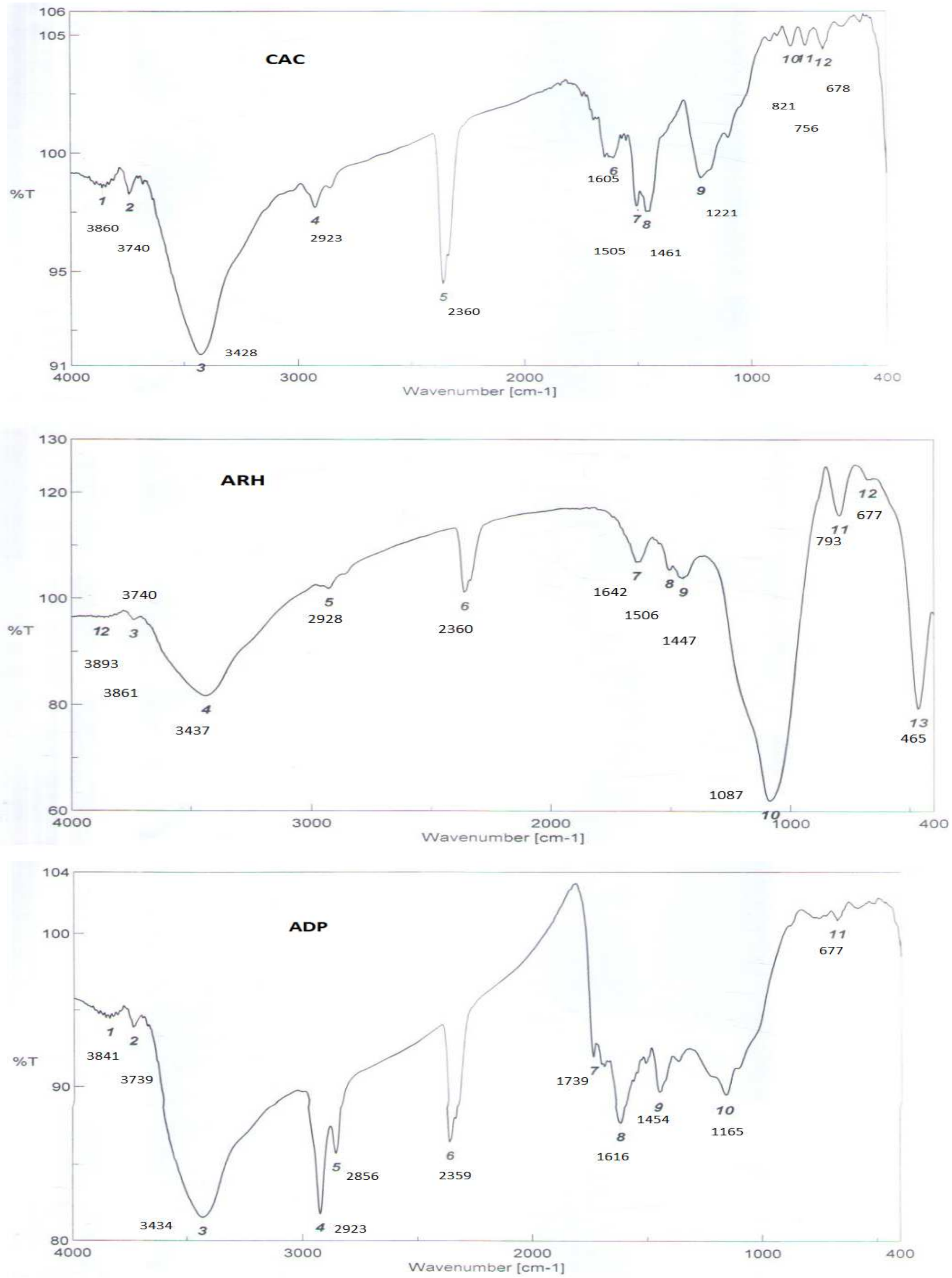

Fig 1. FTIR spectra of commercial activated carbon (CAC) and prepared activated date pits (ADP) and activated rice husks (ARH).

50 mL of wastewater of a known initial COD concentration were magnetically stirred with different weights of adsorbent material (1-10 g), at various mixing time (1- 200 min) at 25 ± 2 °C. During these trials, the COD of both the raw and treated effluent was determined using the closed reflux colorimetric method prescribed by APHA [28]. The COD removal percentage was calculated as follows:

$$\% \text{ COD removal} = [C_0 – C_t/C_0] \times 100 \qquad (1)$$

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

$$q_t = (C_0 – C_t)\, V/ m \qquad (2)$$

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 sorbet at (q_t) is equivalent to amount at equilibrium (q_e).

Table 3. Average Chemical Characteristics of discharged resin production unit effluent

Parameter	*Value*	*Max. Allowable (Standards Decree 44/2000)*
pH	13.0	6-9.5
Temperature	25 °C	43 °C
COD (mg/L)	8210	1100
BOD (mg/L)	3250	600
TSS(mg/L)	1050	800
Nitrate(mg/L)	6.373	100
Phosphate(mg/L)	9.396	25
Oil& Grease (mg/L)	152	100

3 Results and Discussion

3.1 Characterization of CAC, ADP and ARH

FTIR spectroscopy is an important technique used in identifying characteristic surface functional groups on the adsorbent, which in some cases are responsible for the binding of the adsorbate molecules [29]. The surface functional groups of the prepared activated carbon (ADP and ARH) and the commercial activated carbon (CAC) were detected by Fourier transform infrared (FTIR) and the spectra was recorded from 4000 to 400 cm^{-1}. The functional groups were identified by evaluating the spectra using the available literature.

As for the spectra obtained for ARH, , the displayed bands at 3893, 3861 and 3740 cm^{-1} may be attributed to (O–H) vibrations in hydroxyl groups located on alcohol and phenol groups while the latter band may indicate that hydrogen-bonded OH is chemisorbed to water [14, 30]. The broad band between (3000–3700 cm^{-1}) are indicative of Si–OH; 793 and 465 cm^{-1} for Si–H; the silica functional groups of Si–O–Si (1087 cm^{-1}) and band at 677 cm^{-1} may be due to C–O–H twist bending vibrations [12]. An intense peak in the region 1200-1000 cm^{-1} for rice husks was considered to result from superposition of vibrations of the C-O-H bond and Si-O bond in the siloxane (Si-O-Si) groups and the stretching vibrations of silicon-oxygen tetrahedrons as (SiO_4) [31]. The broad band at 3437 cm^{-1} was associated with O-H both free and bonded [32]. The band at 2928 cm^{-1} due to C-H interaction with the surface of carbon; peak at 2360 cm^{-1} C=O stretching from ketones, aldehydes or carboxylic groups, while that at 1642-1506 cm^{-1} may be attributed to C=C stretching, vibration of the aromatic rings or carbonyl groups or C=O stretching all of which are characteristic of hemicelluloses and lignin aromatic groups [33]. The band at 1447 cm^{-1} may be due to C-H asymmetric bending [34, 35].

For ADP, the spectra obtained also indicated the presence of hydroxyl (OH) at 3841 and 3739cm^{-1} which was chemisorbed to water molecules indicated by a strong and broad band at (3434 cm^{-1}) [36]. As well, a broad band between (3000–3700 cm^{-1}) may indicative of Si–OH [12]. The band at 2924 cm^{-1} is associated to the symmetric and asymmetric C–H stretching vibration of aliphatic acids [34]; 2856 cm^{-1} assigned to O-H stretching vibration originating in the molecule [37]; 2359 cm^{-1} denotes C=O [32] and O-H stretching for carboxylic groups [37]; 1739 cm^{-1}: the carbonyl (C=O) groups in phenolic esters, carboxylic acids and conjugated ketonic structures [31,38]: 1454 cm^{-1} may be due to the presence of the OH bending vibration and indicating the presence of phenolic group [32]; 1616 cm^{-1} associated with C=C stretching of alkenes and aromatics or C=O stretching that may be attributed to the hemicelluloses and lignin aromatic groups [33]. The peak at 1165 cm^{-1} represents the stretching of C-O functional group [36] and the band at 677 cm^{-1} associated with C–O-H twist out of plane [12].

Similarly for the CAC spectra, the presence of O-H functional group was indicated by the band at 3860 and 3740 cm^{-1} and 3428 cm^{-1} may indicate chemisorbed water molecules to the OH group [36]; 2923 cm^{-1} symmetric and asymmetric C–H stretching vibration of aliphatic acids [34]; 2360 cm^{-1} denotes C=O [32] and O-H stretching for carboxylic groups [37]; 1606 cm^{-1} due to C-C aromatic stretching [39]; 1500 cm^{-1} for aromatic carbon–carbon stretching vibration [40]; 1461 cm^{-1} due to bending O–H and carboxylate ion –COO- [41]; 1221 cm^{-1} may be associated with C-O-H stretching [39]. The region in between 700- 900 cm^{-1} contains bands related to aromatic, out of plane C-H bending with different degrees of substitution [38] and 821 cm^{-1} may be a reflection of adjacent aromatic C–H stretching [41] and the band at 756 and 677 cm^{-1} are associated with C–O-H twist out of plane [12].

3.2 Effect of Adsorbent Weight, Stirring/Contact Time and pH

Figure 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 89% was obtained using 30 g/L CAC, 83% using 40 g/L ADP and 84% using 60 g/L ARH. Therefore, these optimal adsorbent doses were used for the remainder of the experimental trials. Previous studies have shown that the application of CAC to wastewaters achieved over 90% removal of the non-biodegradable and biodegradable content in wastewater [11, 15, 37, 42-44]. 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 available within each [11]. It was also noted that increasing the adsorbent dose beyond the optimum amount did not increase the % COD removal, however, a slight decrease was observed thereafter. This observation is accordance with the findings of El-Naas et al. [19] 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.

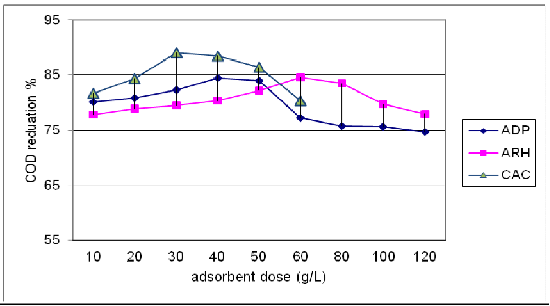

Fig. 2. The effect of adsorbent weight (ADP, ARH and CAC) upon COD reduction % at pH 7; t_{CAC}= 90 min, t_{ADP} =120 min and t_{ARH}= 120 min; T= 25ºC, volume of solution 50 mL, and COD_o = 8210 mg/L.

The effect of stirring/contact time upon the % COD reduction using fixed optimal adsorbent dose of CAC, ADP and ARH is shown in Figure 3. The results indicate that CAC, ADP and ARH achieved a high rate of COD reduction during the initial 60 min. The_maximum COD removal attained using ARH and ADP after 120 min was 88.9% and 90.3%, respectively, while CAC achieved a 92.4% COD reduction at 90 min. These results are within the range of equilibrium times reported for the reduction of COD in some industrial effluents of using CAC [37, 42], for ADP [16] and for ARH [7, 45]. It was also observed that the rate of COD reduction decreased as the optimal time was exceeded for CAC and less significantly for the other material used. Devi [11] and Kumar et al. [37] explained that after the lapse of time the occupied sites were starting to repel the adsorbate molecules in the bulk phase and that the driving force for these molecules to reach the vacant surface sites and get adsorbed was becoming weaker. Ho et al. [46] postulated that the decrease in removal rates was due to the predominance of pore diffusion of adsorbent particles in order to create new sites onto the inner surface of the sorbent material. Faster initial adsorption rates were also attributed to the solute being adsorbed onto the surface of the adsorbent particles until surface saturation was reached [14]. After this point, molecules were to 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 evident with the three adsorbent materials. The curves obtained may reflect that intra-particle diffusion was involved in the current process of adsorption and COD reduction [14,19].

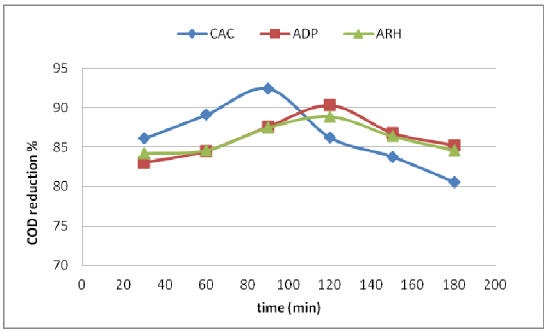

Fig. 3. The effect of varying the stirring/ contact time (min) upon %COD reduction at pH 7, adsorbent weights (30 g/L CAC, 40 g/L ADP and 60 g/L ARH), T= 25ºC, volume of solution 50 mL, and COD_o = 8210 mg/L.

Solution pH is a very important parameter that affects the properties of adsorbate and adsorbent as well as the adsorption process in aqueous solutions [33]. The influence of initial pH on COD reduction in resin wastewater was evaluated through the pH range of 2 to 12 using the optimal dose of CAC, ADP and ARH and the results are depicted in Figure 4. Overall, maximum COD reduction was obtained within the acidic range (pH= 2-4) for the three adsorbents. This is in agreement with the findings of Kabdaşli et al. [47] and Akyol [4] during their treatment of resin containing waters. Although these researchers studied the effect of electro-coagulation upon the final pollutant load, they concluded that the optimal COD and TOC reduction in resin containing water was achieved at pH of 2. This was attributed to the electrostatic interaction between the adsorbed molecule and the adsorbent surface [19, 33]. More explicitly, the amphoteric character of the carbon surface exhibit may influence its adsorption properties as the solution pH varies [19]. Effectively, as the pH increases from the acidic to alkaline, there may be an increased electrostatic repulsion or dispersion between the adsorbate and activated carbon surface and subsequently a decrease in the uptake was observed in the pH range [33]. In conclusion, pH 2 was used as the optimum pH during further experimental work.

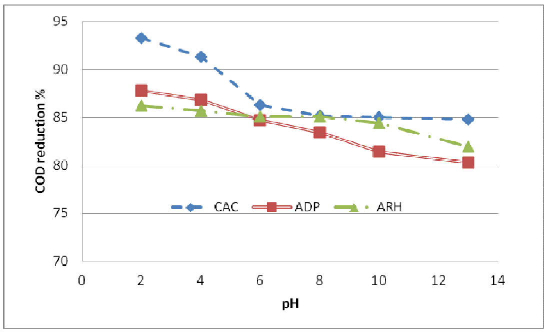

Fig. 4. The effect of varying pH upon %COD reduction, adsorbent weights (30 g/L AC, 40 g/L ADP and 60 g/L ARH), T= 25ºC, volume of solution 50 mL, and COD_o = 8210mg/L.

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 (Figure 5) which indicates the splitting of these variables into 9 clusters all of which were grouped together. Basically, the variable clustering strategy indicated that reduction in effluent phosphate and nitrate was dependent upon the adsorbent weight and solution pH while the optimal treatment time greatly influenced the reduction in wastewater oil and grease. As well, the reduction in these parameters showed as strong interdependency on each other and collectively they were responsible for the decrease and reduction in effluent TSS and BOD contents. On the other hand, while these variables significantly represented the BOD load of this effluent, they represented part and not the total COD content and their reduction was more related to the final BOD load reduction.

Table 4. Main parameters of resin 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	CAC	ADP	ARH	Max. Allowable (Standards Decree 44/2000)
pH	13.0	2.0	2.0	2.0	6-9.5
COD(mg/L)	8210	610	780	900	1100
BOD(mg/L)	3250	256	386	412	600
TSS(mg/L)	1050	19.6	31.4	63.1	800
Nitrate (mg/L)	6.37	0.46	0.94	2.60	100
Phosphate (mg/L)	9.40	1.41	3.34	2.83	25
Oil & Grease (mg/L)	152.0	45.0	90.0	123.0	100

* The current treatment processes 20 m^3/week during the morning 8 hours shift.

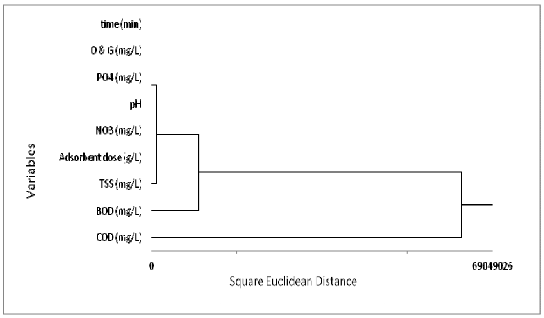

Fig. 5. Dendogram depicting the relationship between the reduced treated effluent main parameters and the optimum adsorbent dose (CAC, ARH and ADP), contact time and solution pH using Ward's methods for minimum variance.

3. 3 Adsorption kinetics

The process adsorption rate was determined for CAC, ADP and ARH by contacting resin wastewater samples with an initial average COD of 8210 mg/L with a variable adsorbent dose (20g/L- 100g/L) and at various time intervals and the results are shown in Table 5. 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 [19, 37] and the intra-particle diffusion [19, 21, 48]. The linearized form of the Lagergren pseudo-first order model is given as:

$$\log (q_e-q_t) = \log q_e - kt/2.303 \qquad (3)$$

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 rate constant for the pseudo-first order adsorption process. This model assumes that the rate of change of adsorbate uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time [49]. As well, in most cases, this adsorption reaction may be preceded by diffusion through a boundary [49]. The experimental data were fitted to equation (3) and the calculated values for k_1 and q_e are provided in Table 5. 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 pseudo second-order rate equation is based upon the sorption capacity of the solid phase and is given as [50]:

$$t/q_t = 1/k_2q_e^2 + t/q_e \qquad (4)$$

where k_2 is the rate constant of second-order adsorption and the slopes of the plots of t/q_t versus 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 reduction of COD onto CAC, ARH and ADP. As well, the calculated values for q_e were close to the experimental values obtained. Thus, it may be concluded that the studied process may be better explained by pseudo-second-order kinetic model better than the first order model. Furthermore, for a pseudo-second order model, it was reported that the rate limiting step may be considered to be a surface adsorption process which involves chemisorption mechanism [19, 37, 49, 50]. Thus, in the current study, COD removal from the investigated wastewater may be regarded as a physicochemical interaction between two phases.

In general, 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 [19]. In many adsorption processes, the adsorbate species may most probably be transported from the bulk of the solution into the solid phase through intra-particle diffusion/transport [7]. For the intra-particle diffusion model, the equation used was [7, 19, 21, 48, 49, 51]:

Table 5. Kinetic parameters calculated for the COD reduction /adsorption onto CAC, ADP and ARH at 25° C, where R^2 is the correlation coefficient

		Pseudo-first-order			Pseudo-second-order			Intra-particle Diffusion		
Adsorbent	Dose (g/L)	K_1 (min^{-1}) x 10^{-3}	q_e (mg/g)	R^2	K_2 (g mg^{-1} min^{-1}) x 10^{-4}	q_e (mg/g)	R^2	K_s (mg g^{-1} $min^{-0.5}$)	I (mg/g)	R^2
CAC	10	6.22	173.78	0.5890	2.36	714.29	0.9883	36.36	331.50	0.9980
	20	2.76	45.80	0.1183	76.45	344.83	0.9908	13.76	220.30	0.9092
	30	3.22	27.39	0.0863	49.00	238.09	0.9914	9.99	148.33	0.9133
	40	2.99	15.30	0.0824	191.10	175.44	0.9906	7.31	110.68	0.8831
	50	2.99	15.30	0.0824	288.00	138.89	0.9910	5.55	89.40	0.8880
ADP	10	11.52	236.76	0.6982	0.86	769.23	0.9920	39.70	280.42	0.9325
	20	11.52	103.68	0.6964	2.07	384.62	0.9941	17.48	167.93	0.9086
	30	11.52	57.23	0.6194	3.78	256.41	0.9952	10.82	124.27	0.8537
	40	12.44	42.13	0.6779	5.34	192.31	0.9964	8.07	96.58	0.8437
	50	11.05	32.62	0.6706	6.84	151.52	0.9959	6.25	77.93	0.8303
ARH	20	13.13	92.64	0.7250	2.08	370.37	0.9950	18.54	144.00	0.7770
	40	15.89	55.06	0.9029	4.30	188.68	0.9978	7.87	89.36	0.8115
	60	14.51	23.71	0.5947	9.59	126.58	0.9973	5.48	63.72	0.7954
	80	9.44	15.54	0.4116	15.47	90.91	0.9937	3.89	47.91	0.8521
	100	7.60	15.00	0.6154	15.75	72.46	0.9930	2.49	41.44	0.7805

Table 6. Isotherm constants and values of R^2 for CAC, ADP and ARH at 25°C and C_o= 8210 mg/ L

	Freundlich Isotherm				Langmuir Isotherm			
Adsorbent	$1/n$ (mg/L)	n (L/mg)	K_f (K mg/g)	R^2	Q_o (mg/g)	b (L/mg)	R_L	R^2
CAC	2.082	0.480	1.413 x10^{-4}	0.8529	625.00	3.07 x 10^{-4}	0.2840	0.9006
ADP	7.055	0.142	1.033 x10^{-19}	0.9092	54.05	7.59 x10^{-4}	0.1380	0.9820
ARH	2.453	0.408	3.74 x10^{-6}	0.6289	111.10	3.69 x10^{-4}	0.2480	0.9590

$$q_t = k_i t^{0.5} + I \qquad (5)$$

where q_t is the fraction of pollutant uptake (mg/g) at time t, k_i is the intra-particle-diffusion rate constant (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 [49, 51]. Furthermore, if the plot of q_t vs. $\sqrt{t}$ passed through the origin, then intra-particle diffusion may be considered as the rate limiting step [7, 21]. Generally, all the plots did not have a zero intercept and were curved to some extent at the initial portion which was followed by a linear portion and a plateau - this was more evident in the case of CAC and ADP. Similar observations were reported by Banat et al. [21], Mane et al. [51], Nandi et al. [49] and El-Naas et al. [19]. This may indicate that surface adsorption and intra-particle diffusion were concurrently operating during the adsorption process [7]. 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 intra-particle diffusion [19, 45, 51]. However, the R^2 values for CAC and ADP ranged between 0.88 - 0.998 and 0.8303-0.9325, respectively, which may denote that the adsorption process onto CAC and ADP tends to proceed as second order process and that that particle/ pore diffusion may be involved but it was not the only rate limiting mechanism [21, 51].

3.4 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 [49, 52-54]. The Freundlich and Langmuir isotherm equations have been extensively to represent the equilibrium adsorption data obtained from activated carbon- organic contaminant systems [37]. 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 [37, 55]. 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 [37, 55]. The linear equation for Freundlich isotherm applied was [21, 37, 48, 56]:

$$\ln q_e = \ln K_f + 1/n \ln C_e \qquad (6)$$

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. A plot of ln qe vs. ln Ce is presented in Figure 6 and the calculations for K_f and (n) for CAC, ADP and ARH removal of COD in the studied wastewater are provided in Table 6. Generally, 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 [7]. They were also used to determine the adsorption capacity of organic pollutants and the extent of COD reduction by adsorbents [11]. Essentially, the larger the K_f value and the smaller the 1/n value indicates that the adsorbent was more effective and that it has a higher the adsorption capacity for the easy uptake of COD from the attested wastewaters [37,53]. Devi [11] 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.

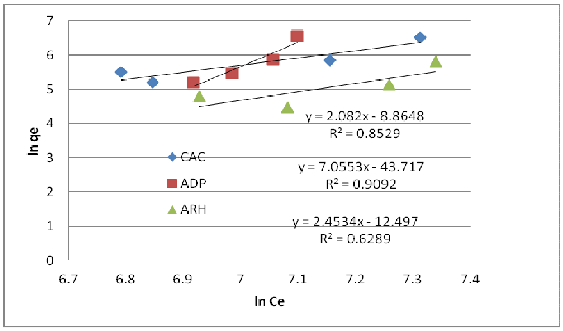

Fig. 6. Freundlich isotherm for COD reduction in resin wastewater onto CAC, ADP and ARH.

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 [7, 14, 37, 56]. The magnitude of *n*, on the other hand, was reported to give an indication of the favorability of adsorption [14, 37, 56] and the higher the *n* signifies that the biosorbent surface was heterogeneous in nature and was high enough for effective separation [53]. 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 [14, 37, 56]. As well, a large value of *1/n* was indicative of a larger change in effectiveness over different equilibrium concentrations [6, 22]. However, it was reported that a value for 1/*n* above 1 was indicative of cooperative adsorption [22, 43]. Concerning the data obtained in this study, the values obtained for *n* were *less* than 1 for all adsorbents, which may be indicate that the adsorbent had poor adsorption characteristics, something that was contrary to the experimental findings. As well, the value obtained for K_f for ADP was significantly smaller in magnitude than that obtained for CAC and ARH which may denote its ineffectiveness for adsorption according to this model.

The Langmuir model was successfully applied to explain real adsorption processes for the reduction of COD using adsorbents by Ahmad and Hameed [14]. 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 [22, 37, 49]. As well, it assumes that all binding sites have the same affinity for adsorption of a single molecular layer and that there was no interaction between absorbent molecules [49]. The linear equation of Langmuir isotherm applied was [37, 56, 57]:

$$1/q_e = 1/(bQ_0 C_e) + 1/Q_0 \qquad (7)$$

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. 7) and the values obtained for the Langmuir constants are shown in Table 6. 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 [42]. In addition, the dimensionless constant separation factor for equilibrium parameter, R_L, is an essential characteristic of the Langmuir isotherm which is defined as [53, 58]:

$$R_L = 1/(1+bC_o) \qquad (8)$$

where *b* is the Langmuir constant (L/mg) and C_o (mg/L) is the initial COD concentration. There are 4 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 $R_L=0$. The values for R_L obtained for the studied system (Table 6) 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 indicated 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 by Langmuir isotherm rather than the Freundlich isotherm model [49].

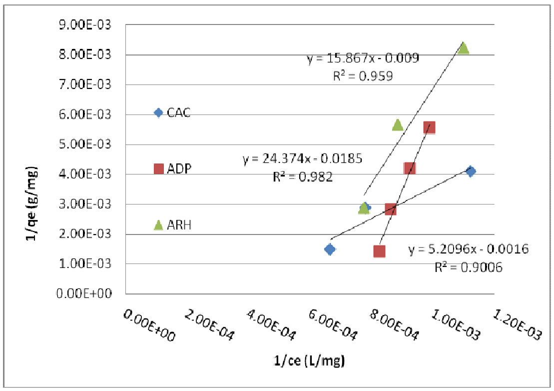

Fig. 7. Langmuir isotherm for COD reduction in resin wastewater onto CAC, ADP and ARH.

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. In the current treatment system, the suspended solids were reduced through coagulation with a polymer and alum after adjusting pH of solution from 13 to 7 in balance tank using H_2SO_4. In the DAF and to aid in the biological treatment process, urea, phosphate and molasses were being added to enhance the degradation of the effluent organic matter. The treated effluent is discharged to public sewer system while sludge formed in a biological reactor, reaction tank and dissolved air flotation unit is thickened and dewatered in the filter press after 5 hours. For an initial COD of 8210 mg/L, the solid content in the 20 m^3/week effluent was estimated to be 120 g/L, which is equivalent to 3600 kg/week. The sludge after filter press is either dumped in the desert or together with the municipal solid waste at the Obour City, which represents an environmental problem.

Resins are widely used in a number of industrial applications. Wastewaters from the production of resin are extremely turbid, white colored that contain high suspended solids content, suspending agents, surface active agents, catalysts, emulsions, small amounts of unreacted monomer and significant amounts of very fine particles of the polymer product. Reduction of this type of waste has become more and more problematic due to the significant annual amounts released to the environment and the increasing cost of treatment. One way to solve this environmental problem has been to reuse this waste and wastewater for other purposes like construction industry in particular the concrete production by incorporating this resin effluent in concrete mixes to replace fresh water [59]. Options to use this sludge after composting as an additive to improve soil quality, add nutrients and promote plant growth were also successfully studied [60].

Furthermore, the use of adsorbents for COD reduction in this wastewater has the advantage of providing an easily filterable sludge that was more eco-friendly and increased its potential for reuse. This may decrease the environmental hazards associated with the current sludge which obtained using conventional precipitation techniques [16]. In effect, sludge obtained using ARH was easily filterable and easily dewatered than the one produced using CAC or ADP. Overall, the technical applicability 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 its activation. On the other hand, the use of adsorbents in the current treatment system may entail a reduction in chemicals use and energy as it will decrease the treatment time from 8 hr to less than 4 hr. As well, it may increase the prospects for water reuse and sludge options for recycle or reuse.

4 Conclusion

During the present study, ADP and ARH were found to be effective adsorbents for the reduction of COD associated with resin production wastewaters effluent compared to commercial CAC. The results indicated that maximum COD reduction of 92.4% was obtained using 30 g/L CAC, 88.9% using 60 g/L ARH and 90.3% using 40 g/L ADP at the optimal pH 2. The optimal time was 90 min, 120 min and 120 min for CAC, ADP and ARH, respectively. 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 either as compost and recycle to with some economical consequences in the future.

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