

Activated carbon from spent coffee grounds as an adsorbent for treatment of water contaminated by aniline yellow dye

Efren Pagalan Jr^a, Michell Sebron^a, Shaina Gomez^a, Sheena Jane Salva^a, Renzey Ampusta^a, Aira Joy Macarayo^a, Cherry Joyno^a, Alexander Ido^a, Renato Arazo^{a,b,*}

^a College of Engineering and Technology, University of Science and Technology of Southern Philippines, Claveria, 9004, Philippines

^b International Affairs Office, University of Science and Technology of Southern Philippines, Claveria, 9004, Philippines

ARTICLE INFO

Keywords:

Adsorption isotherm
Adsorption kinetics
Bioremediation
Colored water treatment
Process optimization
Dye removal

ABSTRACT

One problem that conveys the industrial revolution is the worsening problem of wastewater containing dyes of the effluents from the growing number of dye-producing industries. This study exploited the use of spent coffee grounds (SCG) as a precursor in making activated carbon to treat water contaminated with aniline yellow dye (AYD). The activated carbon, chemically modified using potassium hydroxide, was characterized using Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy. The optimization of the operating parameters in AYD removal was done using Design Expert 7.0 software through the central composite design of response surface methodology to attain the maximum removal efficiency. The result showed that SCG activated carbon has mesopore and micropore structures with honeycomb particle shapes. Several functional groups were identified on the surface, a good indicator as a potential adsorbent. Optimum conditions were found, which are 35 ppm initial AYD concentration, 0.6 g adsorbent dose, and 2.5 h contact time; and achieved a removal of AYD at $88.72 \pm 1.88\%$ with an adsorption capacity of 2.58 mg/g. The adsorption took place heterogeneously in multilayer as revealed in the isotherm analysis with Freundlich as most fitted having R^2 value of 0.9868. The adsorption mechanism is dependent on the physical amount of dye adsorbate or its concentration factor as revealed in kinetic studies with pseudo-first order as the most fitted model having R^2 value of 0.9832. The overall result demonstrated that the activated carbon from SCG is a good material in removing the dye in the contaminated water with huge implications for the future of treating dye-contaminated water from industries.

1. Introduction

Water pollution from industrial activities has become one of the major environmental concerns nowadays. This reality is due to the discharge of untreated water to various receiving water bodies. The release of untreated water from industries had been known to be the primary contributor to water pollution that significantly affects the appearance and ecological balance of aquatic resources (Somasekhara Reddy et al., 2017). One of the problems of industrial wastewater is high dye concentration in the effluent. These dyes and pigments are commonly used as a coloring in textiles, paints, and cosmetics that are known as carcinogenic and mutagenic to life forms (Dakhil, 2013). About 1.6 million tons of dyes are produced annually, as estimated worldwide (Bing et al., 2015). Textile industry consumed dyes about 10,000 tons per year in the production (Gupta et al., 2013), and numerically, about 10–15% of it is being discharged in wastewater (Konicki et al., 2017). Industrial dye-containing wastewater brings

hazards and risks to water quality (Anastopoulos et al., 2017). Dyes in water reduce light penetration and prevent the photosynthesis of aqueous flora (Baldikova et al., 2015). Also, dyes, when mixed with water, can cause illnesses such as allergy, dermatitis, skin irritation, and can even provoke cancer (Dawood and Sen, 2014). One of these is an aniline yellow dye (AYD) that is a highly toxic and cancer-suspect agent.

Continual development of treating dye-contaminated wastewater is among the recent concerns that challenge the academe and the industry. Hence, scientists are searching and continuously developing a more suitable, efficient, and cheaper technique in removing the dye in aqueous solution. Some of the methods in eliminating dye in wastewater include coagulation (Sillanpää et al., 2018), flocculation (Du et al., 2017), oxidation (Tan et al., 2017), and adsorption (Lavecchia et al., 2016). Among these, adsorption using activated carbon is superior because of efficiency (Mu and Wang, 2016), and high removal efficiency (Rattanapan et al., 2017). The activated carbon's high adsorption capacity makes it more efficient in treating dye-contaminated

* Corresponding author at: College of Engineering and Technology, University of Science and Technology of Southern Philippines, Claveria, 9004, Philippines.
E-mail address: roarazo@yahoo.com (R. Arazo).

<https://doi.org/10.1016/j.indcrop.2019.111953>

Received 15 June 2019; Received in revised form 1 November 2019; Accepted 6 November 2019

0926-6690/© 2019 Elsevier B.V. All rights reserved.

wastewater (Franca et al., 2009). Thus, it becomes one of the best available environmental control technologies of the current time (EPA, 2013).

The need to have a low-cost available adsorbent has been increasing in demand (Pavlović et al., 2014). Coffee, with the spent coffee ground (SCG) as wastes, is known as one of the consumed beverages worldwide. The large quantities of SCG that are being generated in coffee industries and consuming communities have been used as organic fertilizer (Campos-Vega et al., 2015). However, scientific evidence of its effectiveness and safety remains unknown. At present, huge volume of SCG is still found in the garbage, causing major environmental issues (Roff, 1973) with 6 million tons needing alternative management (Azouaou et al., 2014). Thus, SCG can be tapped as a source of adsorbent in removing basic dyes and heavy metal ions in wastewater (Zuorro and Lavecchia, 2012). Its potential as the adsorbent is remarkably high, considering its high lignocellulosic component (Ballesteros et al., 2014).

This study utilized the SCG as a source of activated carbon for the adsorption of AYD in aqueous solution. This endeavor would be a value-adding perspective while minimizing wastes in the environment. Furthermore, the study would optimize the removal of AYD through the central composite design (CCD) of the response surface methodology (RSM) using Design Expert 7.0 software. It would optimize the independent factors such as initial dye concentration, contact time, and adsorbent dose to attain high removal efficiency of dye.

2. Materials and methods

2.1. Sorbate and adsorbent preparations

The AYD, with the chemical formula of $C_{12}H_{11}N_3$, was used as a pollutant and was dissolved in the aqueous solution using distilled water. The chemical structure is shown in Fig. 1.

The stock solution was prepared at 1000 ppm (1000 mg/L). The desired concentrations in each run were obtained by dilution of the prepared stock solution (Speight, 2017).

The SCG was collected from Nestle Philippines in Cagayan de Oro City, Philippines. The SCG was processed by following the procedures of the previous study with modification (De Luna et al., 2017) at the Agrivironmental Laboratory of USTP-Claveria, Philippines.

The SCG was pre-treated with hot water, washed with distilled water, drained in a container, and oven-dried at 100 °C for 24 h. After that, SCG was pulverized, sieved through 40–80 mm mesh size, and soaked in potassium hydroxide (KOH) at 1 mol/L concentration with a ratio of 1:5 (g of SCG/mL KOH concentration) for 24 h at 25 °C. The mixture was dried at 105 °C for 12 h and carbonized at 500 °C for 30 min in a muffle furnace (LAB TECH el LEF-304P-2). Then, the produced adsorbents were treated with 0.1 mol/L hydrochloric acid (HCL) and washed with distilled water until pH 7 was obtained. The slurry was dried at 105 °C until a constant mass was attained.

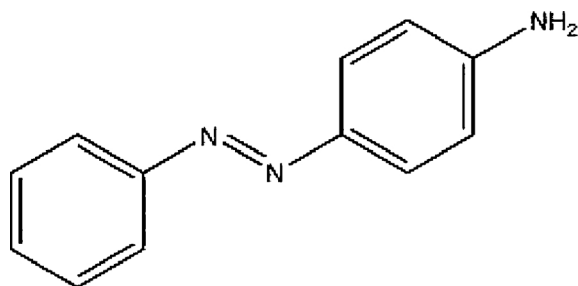


Fig. 1. Chemical structure of aniline yellow dye.

2.2. Methods of determining physical and chemical properties of the adsorbent

The physical and chemical properties of the activated carbon from SCG were analyzed through Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) methods (Kwiecińska et al., 2019; Sharma and Bhardwaj, 2019; Yurdakal et al., 2019). The analyses were conducted at the Department of Mining, Metallurgical, and Materials Engineering and Analytical Service Laboratory, and Institute of Chemistry, University of the Philippines Diliman, Quezon City, Philippines. The scan of the sample via FTIR (Shimadzu Prestige 21FTIR Spectrophotometer) was obtained using an attenuated total reflectance (Miracle ATR, single reflectance, Pike Technologies).

2.3. Experimentation

Preliminary experiments through the parametric study were conducted to determine the most influential factors that affect the removal of AYD using AC from SCG. Among the factors considered in the parametric study were initial AYD concentration, temperature, adsorbent dose, pH, and contact time. From the parametric runs, the three most influential factors that showed significant effects on AYD removal were chosen, i.e., initial dye concentration, adsorbent dose, and contact time. The other two variables were held as they were: room temperature (25 ± 3 °C), and mixture pH (7–9).

The ranges of the values of operating factors are shown in Table 1. Through the RSM, particularly the CCD of Design Expert 7.0 software, 20 runs with varied combinations of chosen factors (initial dye concentration, adsorbent dose, and contact time) were generated and used as the basis in the experimental runs.

2.4. Modeling and optimization

The percentage of AYD removal was computed using Eq. 1 where removal is the percentage of AYD that is being removed in aqueous solution, C_0 is the initial dye concentration (mg/L), and C is the dye concentration at any time (mg/L).

$$\% \text{ removal} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

The effects of adsorbent dose, initial concentration of dye, and contact time were analyzed through analysis of variance (ANOVA), and the best model was determined. Numerical optimization was employed to determine possible combinations of operating factors that would result in optimum dye removal efficiency. The suggested solution of the numerical optimization with high desirability was validated through actual runs in the laboratory.

In the analysis, with a level of significance at 0.05, the significant factors were determined. The effects of the factors in the removal of dye were analyzed and presented through contour plots and 3D models generated from Design Expert 7.0 software.

2.5. Adsorption isotherm and kinetic models

The experiment on isotherm models was based on the optimum values determined in batch adsorption experiments. In the

Table 1
Experimental range and levels of independent factors.

Factor	Coded level				
	-2	-1	0	1	2
Initial concentration (ppm)	20	25	30	35	40
Adsorbent dose (g)	0.3	0.6	0.9	1.2	1.5
Contact time (h)	2.0	2.5	3.0	3.5	4.0

experimental runs, the optimum adsorbent dose and contact time were held constant while initial concentration was varied.

The residual dye concentration was determined by the estimation of the absorbance of the supernatant solution using a spectrophotometer. The adsorption capacity (Q) was computed using Eq. 2 where Q is the adsorption capacity, C_o is initial dye concentration, C is dye concentration at any time, V is the sample volume, and m is the mass of adsorbent.

The data were fitted to Langmuir and Freundlich models. The Langmuir isotherm model was calculated using Eq. (3) where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_o is the adsorption capacity (mg/g), b is the energy of adsorption (L/mg), and C_e is the equilibrium concentration of the adsorbate (mg/L). The Freundlich isotherm model was computed using Eq. (4), where K_F is the Freundlich capacity factor and $1/n$ is the intensity parameter.

$$Q = \frac{(C_o - C) v}{m} \quad (2)$$

$$\frac{1}{q_e} = \left[\frac{1}{bQ_o} \right] \frac{1}{C_e} + \frac{1}{Q_o} \quad (3)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

$$\ln C_t = \ln C_o - k_1 t \quad (5)$$

$$\frac{1}{C_t} = \frac{1}{C_o} + k_2 t \quad (6)$$

The experimentation of the kinetic model was based on the optimal operating conditions with variable contact time. The collected data was fitted to pseudo-first and pseudo-second order kinetic models. The equations of pseudo-first order and pseudo-second order kinetic are shown in Eqs. (5) and (6) where C_o is the initial concentration of AYD (mg/L), C_t is the AYD concentration at any reaction time (mg/L), t is the contact time (h), K_1 is the first-order rate constant (h^{-1}), and K_2 is the rate constant of second-order (h/L).

3. Results and discussion

3.1. Physical and chemical properties of activated carbon from SCG

The activated carbon from SCG has mesoporous and microporous structures (Fig. 2), a strong indication that KOH served successfully in chemically modifying the physical structure of the biomass. The same phenomena were observed from the KOH-prepared activated carbon from banana peels (Thuan et al., 2016).

The heterogeneous activated carbon in a honeycomb shape, from SCG, is a good determinant of a quality material owing that it can trap the dye adsorbate into the adsorbent surface. A similar phenomenon was observed from the production of activated carbon from coconut husk using KOH (Tan et al., 2008) and using nitric acid from the mahogany pod (Sumalinog et al., 2012). It implied that the prepared activated carbon from SCG via KOH activation could compete with other precursors in adsorbing dyes in the effluent.

The determination of the present functional groups on the adsorbent surface was investigated through FTIR spectra ranging from 500-4000 cm^{-1} (Fig. 3), and the adsorbent spectral characteristics are summarized (Table 2). Generally, wavelength peaks suggested the presence of alcohol, hydroxyl, alkane, alkene, alkyne, aromatic, and ether groups.

The O-H deformation was observed at the range of 1400-1320 cm^{-1} showing the presence of the hydroxyl groups with the actual peak of 1372.39 cm^{-1} . The O-H stretch bond determined the presence of hydrogen-bonded hydroxyl groups (from carboxyl, phenols, and alcohol) at the range of 3450-3255 cm^{-1} with the actual peak of 3342.25 cm^{-1} (Chou et al., 2012). The C-H stretch bond determined the presence of alkane groups at 3000-2900 cm^{-1} with the actual peak found at 2927.94

cm^{-1} . The C-H out of plane bend was observed at the 750-665 cm^{-1} with the actual peaks of 729.09 cm^{-1} showing the presence of alkanes. The C=C bond wavelength peaks was observed at 1620.23 cm^{-1} and 1462.07 cm^{-1} suggesting the presence of alkenes and aromatic groups. The peaks indicated that the prepared activated carbon from SCG developed organic matter making this several functional groups exist (Ma and Ouyang, 2013). The C-O stretch bond showed the presence of ether groups that were observed at 1240-1100 cm^{-1} with the actual peaks at 1238.45 cm^{-1} and 1155.58 cm^{-1} . The CC≡ stretch bond at 2140-2085 cm^{-1} shows the presence of alkynes with the actual peak at 2100.50 cm^{-1} . Additionally, the spectrum peak at 2140-2100 cm^{-1} displays the presence of the acetylenic (alkyne) groups (Coates, 2000). The outcome showed that activated carbon from SCG has similar components as cited by past studies mentioned above, signifying its potential to adsorb the AYD molecules efficiently from aqueous solution.

3.2. Percent removal of AYD using SCG activated carbon

The percentage removal of AYD in aqueous solution ranges from 75.01% to 95.52% (Table 3). The likely increase and decrease of AYD removal were due to the interaction effect of the operating factors. A relevant result was reported postulating the interactive effects of the operating factors in dye removal from wastewater (Lim et al., 2016). This result implied that the chosen operating factors have corresponding influences on the removal of AYD, using SCG activated carbon, from aqueous solution.

3.3. Predictive model of AYD removal using SCG activated carbon

The analysis of the data obtained from the experimental runs revealed the surface quadratic equation (Eq. 7) as the most fitted model to correctly predict the percent removal of AYD, as affected by chosen operating factors, using SCG activated carbon as adsorbent (Eq. 7).

$$y = 2.170 - 0.710A + 72.328B + 51.296C - 0.312AB - 0.935AC - 3.117BC + 0.056A^2 - 30.226B^2 - 4.341C^2 \quad (7)$$

where y is the predicted percent dye removal of AYD in aqueous solution while A , B and C are the values of the chosen factors such as initial dye concentration (ppm), adsorbent dose (g), and contact time (h); respectively.

The quadratic equation indicated that, if the value of initial dye concentration (A) alone is increased, the percent dye removal decreases. Similarly, the increase of adsorbent dose (B) and contact time (C), when taken singly, results in higher percent dye removal. However, when these factors interact together, one factor may favor the other, which developed a high percent of dye removal or otherwise. The interaction between initial concentration and adsorbent dose did not favor better percent removal, having a negative coefficient. The same interaction had been observed between initial concentration and contact time because increasing both factors would lower dye removal. It implied that the chosen parameters had antagonistic interactions with each other during the adsorption process resulting in low percent dye removal.

On the other hand, the squared value of initial dye concentration favored the removal of AYD in the aqueous solution having a positive coefficient while the squared values of adsorbent dose and contact time did not favor the AYD removal having a negative coefficient in the model. The opposing effects, as shown in terms of the quadratic equation, made the model more important and meaningful. It can give a better predictive outcome.

The quadratic equation generated by CCD was validated according to the results in actual runs, as shown in Table 4. The reliability of the quadratic model was determined through the analysis of variance (Table 5).

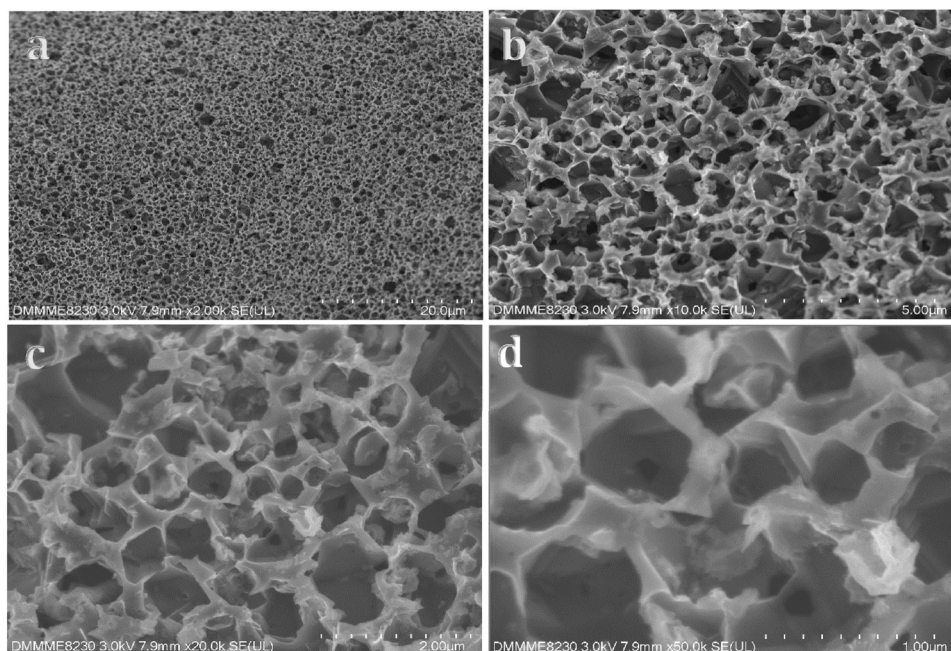


Fig. 2. SEM micrographs of activated carbon from spent coffee grounds with magnifications of (a) 20 μm , (b) 5 μm , (c) 2 μm , and (d) 1 μm .

The significant model F-value of 17.51 shows that it had only a 0.01% chance that this large model F-value could occur due to random data changes. The result showed that the model p-value was significant, having a 0.01% chance of error in predicting the percent removal of AYD using SCG activated carbon. By using the equation, it can be deduced that the result can be 99.99% reliable and accurate in estimating the percent removal of AYD. The lack of fit F-value of 0.23 implied that the lack of fit was not significant relative to the pure error. There is a 93.51% chance that a lack of fit F-value this large could occur due to random data changes. It means that the insignificant lack of fit p-value of 0.9351 was good. Further, the high coefficient of determination (R^2) value of 0.9403 supported that the model in predicting the percent removal of the AYD is efficient. Thus, 94.03% justified that the factor of the data can be explained as produced by the model.

3.4. Significant interactive effects of the chosen factors in the removal of AYD

The interactive effects of independent factors such as initial concentration, adsorbent dose, and contact time in the removal of AYD in

Table 2

FTIR functional groups of the SCG activated carbon.

Functional group	Wavelength peak (cm^{-1})		Bond
	Range	Actual	
Alcohol (hydrogen-bonded hydroxyl groups)	3450-3255	3342.65	O-H stretch
Alcohol (hydroxyl)	1400-1320	1372.39	O-H deformation
Alkane	3000-2900	2927.94	C-H stretch
Alkane	750-665	729.09	C-H out-of-plane bend
Alkene	1650-1610	1620.23	C=C stretch
Aromatic	1500-1300	1462.07	C=C stretch
Alkyne	2140-2085	2100.50	CC \equiv stretch
Ether	1210-1100	1155.58	C-O stretch
Ether	1240-1200	1238.45	C-O stretch

the adsorption process were determined. The ANOVA revealed that only the initial concentration and contact time (AC) have significant interactive effects on the removal of AYD in aqueous solution. Other

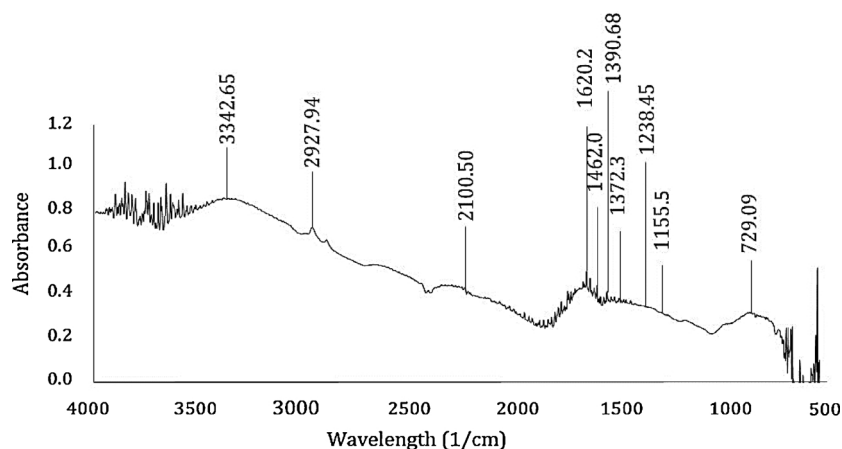


Fig. 3. FTIR spectrum of SCG activated carbon.

Table 3
Percent removal of AYD using activated carbon from SCG.

Run	Operating factor			% AYD removal
	Initial AYD conc'n. (ppm)	Adsorbent dose (g)	Contact time (h)	
1	30	0.3	3.0	75.21
2	30	0.9	3.0	88.29
3	30	1.5	3.0	75.21
4	30	0.9	3.0	83.93
5	30	0.9	3.0	88.29
6	30	0.9	2.0	88.29
7	30	0.9	3.0	83.93
8	30	0.9	3.0	83.93
9	35	0.6	2.5	86.23
10	30	0.9	3.0	88.29
11	40	0.9	3.0	87.95
12	20	0.9	3.0	95.52
13	35	0.6	3.5	78.75
14	25	1.2	2.5	85.95
15	25	0.6	3.5	85.95
16	25	0.6	2.5	85.95
17	25	1.2	3.5	85.95
18	25	1.2	3.5	75.01
19	35	1.2	2.5	86.23
20	30	0.9	4.0	75.21

Table 4
Actual vs. predicted AYD removal from aqueous solution.

Run	Operating factor			AYD removal (%)	
	Initial concentration (ppm)	Adsorbent dose (g)	Contact time (h)	Actual	Predicted
1	30	0.3	3.0	75.21	75.71
2	30	0.9	3.0	88.29	86.12
3	30	1.5	3.0	75.21	74.77
4	30	0.9	3.0	83.93	86.12
5	30	0.9	3.0	88.29	86.12
6	30	0.9	2.0	88.29	87.39
7	30	0.9	3.0	83.93	86.12
8	30	0.9	3.0	83.93	86.12
9	35	0.6	2.5	86.23	87.05
10	30	0.9	3.0	88.29	86.12
11	40	0.9	3.0	87.95	87.67
12	20	0.9	3.0	95.52	95.85
13	35	0.6	3.5	78.75	77.71
14	25	1.2	2.5	85.95	86.94
15	25	0.6	3.5	85.95	85.54
16	25	0.6	2.5	85.95	85.53
17	25	1.2	3.5	85.95	85.07
18	25	1.2	3.5	75.01	75.37
19	35	1.2	2.5	86.23	86.59
20	30	0.9	4.0	75.21	76.17

interacting variables (AB and BC) do not statistically show significant interactive effects in AYD removal using SCG activated carbon. Hence, the interactive effect of AC is the only one presented (Fig. 4).

Based on the graph, the increase of contact time at higher dye concentration resulted in a decrease in the percent AYD removal. At lower contact time, the dye uptake was rapid due to the number of available active sites, and it decreased as the time increased due to incrementally occupied adsorbent sites (Menya et al., 2018). Additionally, with an increase of initial dye concentration, it developed saturation on the adsorbent sites yielding to lower adsorption removal percentage (Kyzas et al., 2013). On the other hand, as initial concentration increased, the percent dye removal decreased at higher contact time. The increased in initial dye concentration accumulated a mass of dye in the adsorbate, leading to the diffusion of dyes in the solution making the adsorption removal slower (Ozacar and Sengil, 2005). The best condition of both parameters was in lower contact time

Table 5
ANOVA showing the reliability of the quadratic surface model in estimating AYD removal using SCG activated carbon.

Source	Sum of squares	df	Mean square	F value	p-value	Prob > F
Model	551.45	9	61.27	17.51	< 0.0001	
A-initial concentration	66.91	1	66.91	19.12	0.0014 ^a	
B-adsorbent dose	0.87	1	0.87	0.25	0.6280 ^b	
C-contact time	125.78	1	125.78	35.94	0.0001 ^a	
AB	1.75	1	1.75	0.50	0.4958 ^b	
AC	43.71	1	43.71	12.49	0.0054 ^a	
BC	1.75	1	1.75	0.50	0.4958 ^b	
A ²	50.05	1	50.05	14.30	0.0036 ^a	
B ²	186.06	1	186.6	53.16	<0.0001 ^a	
C ²	29.62	1	29.62	8.46	0.0156 ^a	
Residual	35.00	10	3.50			
Lack of fit	6.48	5	1.30	0.23	0.9351 ^b	
Pure error	28.51	5	5.70			
Cor total	586.45	19				

a = significant; b = not significant.

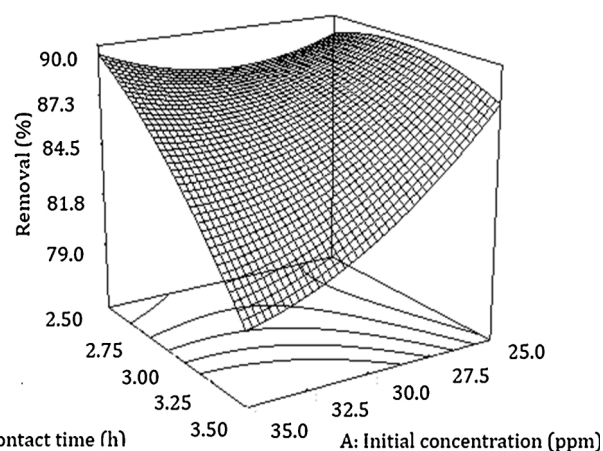


Fig. 4. 3D response surface on the effect of initial concentration and contact time

and concentration, producing higher percent removal.

3.5. Optimum conditions on AYD removal using activated carbon from SCG

The validation runs were conducted with the given optimum conditions of the determining factors. The suggested optimum values of CCD were 35 ppm initial AYD concentration, 0.6 g adsorbent dose, and 2.5 h contact time having the optimum predicted AYD removal of 87.05%. The actual verification runs were conducted, and the result was 88.72% \pm 1.88% AYD removal. The result indicated a very close value of the predicted (87.05%) and actual (88.72 \pm 1.88%) AYD removal with a percent error of 1.88%. At optimum conditions, the adsorption capacity was calculated at 2.58 mg/g, which means that 1 g of SCG activated carbon can remove 2.58 mg of AYD in aqueous solution. The optimization and validation results on the removal of AYD in aqueous solution are shown in Table 6.

The adsorption capacity of the SCG activated carbon showed comparable results on the removal of synthetic dyes on wastewater effluent like in elimination of malachite green using ortho-phosphoric-activated SCG with adsorption capacity of 6.76 mg/g (Lim et al., 2016). To some extent, the adsorption capacity of SCG activated carbon to heavy metals is much higher like of Cd (II) with 70 mg/g, and Cr(VI) of 45 mg/g (Kyzas, 2012). It implied that activated carbon from SCG has the potential to be an alternative source of activated carbon precursor on

Table 6
Optimization and validation results on AYD removal via adsorption.

Experiment	Initial conc'n (ppm)	Factor Adsorbent dose (g)	Contact time (h)	AYD removal (%)
CCD ^a	35	0.6	2.5	87.05
Validation	35	0.6	2.5	88.72 ± 1.88
Biosorbent char ^b	35	0.6	2.5	41.36 ± 2.16

^a Optimization criteria: in range initial concentration (25–35 mg/L); minimize adsorbent dose and contact time; maximize AYD removal.

^b Control run using non-activated SCG char.

treating wastewater containing dye, toxic waste, and other heavy metals in the effluent.

Additionally, the removal efficiency of the KOH-modified and activated adsorbent (88.72%) is far better than the biosorbent char (41.36%). This result implied that chemical activation strengthens the capacity of the materials twice that would eventually increase its overall adsorption capacity. A similar study (Viotti et al., 2019) on the removal of diclofenac using *Moringa oleifera* pods showed higher removal efficiency of the activated material (71 0.15 mg/g) compared to the inactivated one (60.81 mg/g).

3.6. Isotherm and kinetic studies

Isotherm experiments were conducted using the optimum conditions of 0.6 g adsorbent dose and 2.5 h contact time; while varying the AYD concentration (ppm) at 30, 35, 40, 45, and 50.

As a result, the most fitted isotherm model on predicting the percent removal of AYD was Freundlich model having a R^2 regression value of 0.9868 (Fig. 5b) compared to the Langmuir model having a R^2 value of 0.9498 (Fig. 5a). The Freundlich isotherm model has, therefore, 98.68% reliability to explain the mechanism of AYD removal. This result explained a multilayer and heterogeneous adsorption that occurred on the

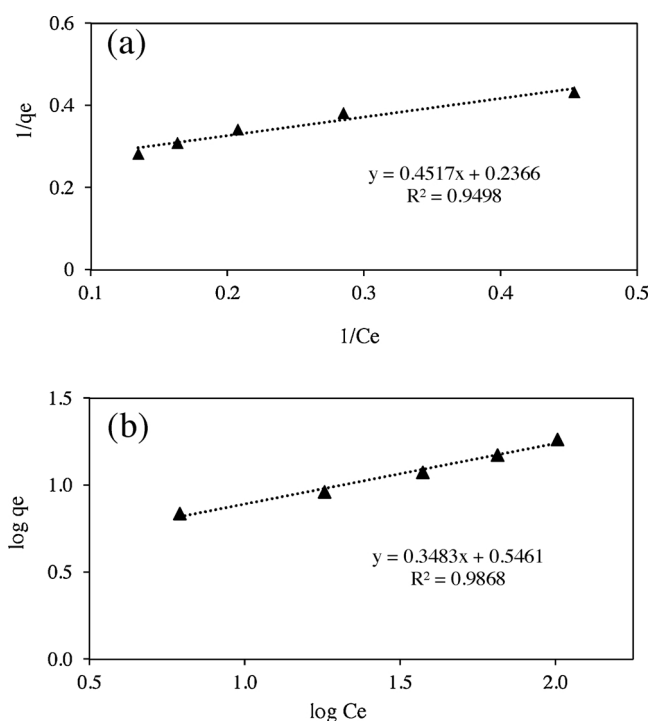


Fig. 5. Isotherm plots of (a) Langmuir, and (b) Freundlich models all done with 0.6 g adsorbent, 2.5 h contact time, and $n = 3$.

Table 7
Isotherm model constants and correlation coefficients.

Langmuir		Freundlich	
Factor	Value	Factor	Value
b , mg	9.3570	$1/n$	0.3483
Q_0 , mg/g	4.2265	K_f	2.2299
R^2	0.9498	R^2	0.9868

non-uniform energy level of the adsorption surface (Song et al., 2013). This indicated that, on the treatment process, the reaction developed a non-uniform level of adsorbate into the adsorbent surface plane leading to multilayer adsorption (Rattanapan et al., 2017). It signified that there were a lot of adsorbate molecules migration on the surface plane leading to a heterogeneous nature in the adsorption process. Table 7 shows the isotherm model constants and correlation coefficients.

In a kinetic study, the experimental runs were conducted to determine how fast the adsorption process took place with the given optimum conditions of the operating parameters varying the contact time at 0.5, 1, 1.5, 2, 2.5, and 3.0 h.

Based on the result, the most fitted kinetic model was the pseudo-first order having an R^2 value of 0.9832 (Fig. 6a). This means that the first order was 98.32% reliable on the accuracy of the experimental study compared to pseudo-second order having a R^2 value of 0.8918 or 89.18% (Fig. 6b). The result indicated that the rate of adsorption is dependent on the concentration factor or the physical amount of the adsorbate, unlike the pseudo-second order that relied on the available adsorbent sites and the required time to attain equilibrium saturation on the adsorbent surface (Liu, 2008). It signified that dye adsorbate amount had a significant effect on the rate of adsorption during the treatment process. A similar study using commercial coffee wastes to adsorb heavy metals revealed the best correlation in pseudo-first order with R^2 value of 0.996 (Kyzas, 2012). Table 8 shows the kinetic model constants and correlation coefficients.

4. Conclusion

The study was conducted to determine the efficiency of activated carbon from the spent coffee ground as a potential precursor to

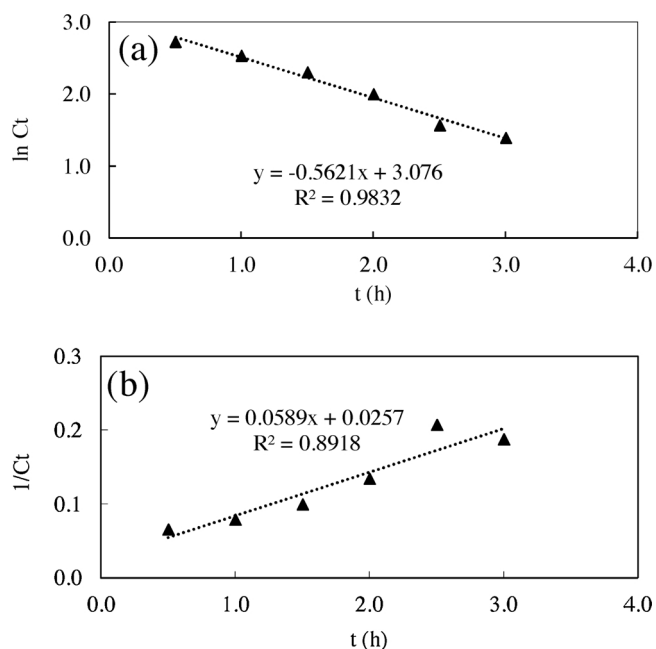


Fig. 6. Kinetic plots of (a) pseudo-first order, and (b) pseudo-second order all done with 0.6 g adsorbent, 35 ppm AYD concentration, and $n = 3$.

Table 8
Kinetic model constants and correlation coefficients.

Pseudo-first order		Pseudo-second order	
Factor	Value	Factor	Value
K_1, min^{-1}	0.5621	$K_2, \text{min/L}$	0.0589
$\ln C_0$	3.076	$1/C_0, \text{mg/L}$	0.0257
R^2	0.9832	R^2	0.8918

removing aniline yellow dye in aqueous solution through adsorption. The current work arrived at the following conclusions:

- 1 SCG activated carbon produced a mesopore and micropore structure with honeycomb shape showing great potential on trapping the AYD dye adsorbate onto the adsorbent surface;
- 2 SCG activated carbon revealed several functional groups such as alcohol, hydroxyl, alkane, alkene, alkyne, aromatic and ether;
- 3 Percent removal of AYD using activated carbon from SCG in aqueous solution ranges from 75.01% to 95.52%;
- 4 3D model graph and ANOVA result suggested that the initial concentration and contact time have significant effects on the removal of AYD in aqueous solution. While the adsorbent dose showed a minimal effect on determining the percent AYD removal;
- 5 Optimum removal of AYD of 87.05% can be obtained at 35 ppm initial dye concentration, 0.6 g adsorbent dose, and 2.5 h contact time with an adsorption capacity of 2.58 mg/g.
- 6 Adsorption took place in multilayer and non-uniform rate as described by most fitted Freundlich model; and
- 7 Rate of adsorption on AYD onto activated carbon from SCG is best described by the pseudo-first order explaining that adsorption depends on the physical amount of dye adsorbate.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors are grateful to the University of Science and Technology of Southern Philippines in Claveria, Philippines, for the support in the conduct of the study.

References

- Anastopoulos, I., Karamesouti, M., Mitropoulos, A.C., Kyzas, G.Z., 2017. A review for coffee adsorbents. *J. Mol. Liq.* 229, 555–565. <https://doi.org/10.1016/j.molliq.2016.12.096>.
- Azouaou, N., Sadaoui, Z., Mokaddem, H., 2014. Removal of lead from aqueous solution onto untreated coffee grounds: a fixed-bed column study. *Chem. Eng. Trans.* 38, 151–156. <https://doi.org/10.3303/CET1438026>.
- Baldikova, E., Safarikova, M., Safarik, I., 2015. Organic dyes removal using magnetically modified rye straw. *J. Magn. Magn. Mater.* 380, 181–185. <https://doi.org/10.1016/j.jmmm.2014.09.003>.
- Ballesteros, L.F., Teixeira, J.A., Mussatto, S.I., 2014. Chemical, functional, and structural properties of spent coffee grounds and coffee silverskin. *Food Bioprocess Technol* 7, 3493–3503. <https://doi.org/10.1007/s11947-014-1349-z>.
- Bing, K., Vakili, M., Amini, B., Eong, P., Zuhairi, A., Salamatinia, B., 2015. Adsorption of dyes by nanomaterials: recent developments and adsorption mechanisms. *Sep. Purif. Technol.* 150, 229–242. <https://doi.org/10.1016/j.seppur.2015.07.009>.
- Campos-Vega, R., Loarca-Piña, G., Vergara-Castañeda, H.A., Oomah, B.D., 2015. Spent coffee grounds: a review on current research and future prospects. *Trends Food Sci. Technol.* 45, 24–36. <https://doi.org/10.1016/j.tifs.2015.04.012>.
- Chou, W.-L., Wang, C.-T., Huang, K.-Y., Chang, Y.-C., Shu, C.-M., 2012. Investigation of indium ions removal from aqueous solutions using spent coffee grounds. *Int. J. Phys. Sci.* 7, 2445–2454. <https://doi.org/10.5897/IJPS12.192>.
- Coates, J., 2000. Interpretation of infrared spectra, a practical approach. In: Meyers, R.A. (Ed.), *Encyclopedia of Analytical Chemistry*. John Wiley & Sons Ltd, Newtown, USA, pp. 10815–10837.
- Dakhil, I.H., 2013. Adsorption of methylene dye from wastewater by spent tea leaves. *J. Kerbala Univ.* 11, 5–14.
- Dawood, S., Sen, T.K., 2014. Review on dye removal from its aqueous solution into alternative cost effective and non-conventional adsorbents. *Int. J. Chem. Process. Eng.* 1, 1–11.
- De Luna, M.D.G., Murniati Budianta, W., Rivera, K.K.P., Arazo, R.O., 2017. Removal of sodium diclofenac from aqueous solution by adsorbents derived from cocoa pod husks. *J. Environ. Chem. Eng.* 5, 1465–1474. <https://doi.org/10.1016/j.jece.2017.02.018>.
- Du, Q., Wei, H., Li, A., Yang, H., 2017. Evaluation of the starch-based flocculants on flocculation of hairwork wastewater. *Sci. Total Environ.* 601–602, 1628–1637. <https://doi.org/10.1016/j.scitotenv.2017.06.029>.
- EPA, U., 2013. *Monitoring by Control Technique - Activated Carbon Adsorber*. pp. 1–2.
- Franca, A.S., Oliveira, L.S., Ferreira, M.E., 2009. Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds. *Desalination* 249, 267–272. <https://doi.org/10.1016/j.desal.2008.11.017>.
- Gupta, V.K., Kumar, R., Nayak, A., Saleh, T.A., Barakat, M.A., 2013. Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. *Adv. Colloid Interface Sci.* 193–194, 24–34. <https://doi.org/10.1016/j.cis.2013.03.003>.
- Koniccki, W., Aleksandrak, M., Moszyński, D., Mijowska, E., 2017. Adsorption of anionic azo-dyes from aqueous solutions onto graphene oxide: equilibrium, kinetic and thermodynamic studies. *J. Colloid Interface Sci.* 496, 188–200. <https://doi.org/10.1016/j.jcis.2017.02.031>.
- Kwiecińska, B., Pusz, S., Valentine, B.J., 2019. Application of electron microscopy TEM and SEM for analysis of coals, organic-rich shales and carbonaceous matter. *Int. J. Coal Geol.* 211, 1–13. <https://doi.org/10.1016/j.coal.2019.05.010>.
- Kyzas, G.Z., 2012. Commercial coffee wastes as materials for adsorption of heavy metals from aqueous solutions. *Materials (Basel)*. 5, 1826–1840. <https://doi.org/10.3390/ma5101826>.
- Kyzas, G.Z., Bikiaris, D.N., Kostoglou, M., Lazaridis, N.K., 2013. Copper removal from aqueous systems with coffee wastes as low-cost materials. *E3S Web Conf.* 1 (25004), 1–5. <https://doi.org/10.1051/e3sconf/20130125004>.
- Lavecchia, R., Medici, F., Patterer, M.S., Zuurro, A., 2016. Lead removal from water by adsorption on spent coffee grounds. *Chem. Eng. Trans.* 47, 295–300. <https://doi.org/10.3303/CET1647050>.
- Lim, J.W., Lam, K.Y., Bashir, M.J.K., Yeong, Y.F., Lam, M.K., Ho, Y.C., 2016. Spent coffee grounds-based activated carbon preparation for sequestering of malachite green. *AIP Conf. Proc.* 1787, 1–5. <https://doi.org/10.1063/1.4968087>.
- Liu, Y., 2008. New insights into pseudo-second-order kinetic equation for adsorption. *Colloids Surfaces A Physicochem. Eng. Asp.* 320, 275–278. <https://doi.org/10.1016/j.colsurfa.2008.01.032>.
- Ma, X., Ouyang, F., 2013. Adsorption properties of biomass-based activated carbon prepared with spent coffee grounds and pomelo skin by phosphoric acid activation. *Appl. Surf. Sci.* 268, 566–570. <https://doi.org/10.1016/j.apsusc.2013.01.009>.
- Menya, E., Olupot, P.W., Storz, H., Lubwama, M., Kiros, Y., 2018. Production and performance of activated carbon from rice husks for removal of natural organic matter from water: a review. *Chem. Eng. Res. Des.* 129, 271–296. <https://doi.org/10.1016/j.cherd.2017.11.008>.
- Mu, B., Wang, A., 2016. Adsorption of dyes onto palygorskite and its composites: a review. *J. Environ. Chem. Eng.* 4, 1274–1294. <https://doi.org/10.1016/j.jece.2016.01.036>.
- Ozacar, M., Sengil, I.A., 2005. Adsorption of metal complex dyes from aqueous solutions by pine sawdust. *Bioresour. Technol.* 96, 791–795. <https://doi.org/10.1016/j.biortech.2004.07.011>.
- Pavlović, M.D., Buntić, A.V., Marinković, S.S.Š., Antonović, D.G., Milica, D., Radovanović, N.R., Branković, S.I.D., 2014. Spent coffee grounds as adsorbents for pesticide removal from its aqueous solutions. In: *International Conference on Civil, Biological and Environmental Engineering*. International Institute of Chemical, Biological and Environmental Engineering, Turkey. pp. 60–65. <https://doi.org/10.15242/IICBE.C514541>.
- Rattanapan, S., Srikram, J., Kongsune, P., 2017. Adsorption of methyl orange on coffee grounds activated carbon. *Energy Procedia* 138, 949–954. <https://doi.org/10.1016/j.egypro.2017.10.064>.
- Roff, D.A., 1973. An examination of some statistical tests used in the analysis of mark-recapture data. *Oecologia* 12, 35–54. <https://doi.org/10.1007/BF00345469>.
- Sharma, V., Bhardwaj, A., 2019. Scanning electron microscopy (SEM) in food quality evaluation. *Evaluation Technologies for Food Quality*. Woodhead Publishing Series in Food Science, Technology and Nutrition, New Delhi, India, pp. 743–761. <https://doi.org/10.1016/B978-0-12-814217-2.00029-9>.
- Sillanpää, M., Ncibi, M.C., Matilainen, A., Vepsäläinen, M., 2018. Removal of natural organic matter in drinking water treatment by coagulation: a comprehensive review. *Chemosphere* 190, 54–71. <https://doi.org/10.1016/j.chemosphere.2017.09.113>.
- Somasekhara Reddy, M.C., Nirmala, V., Ashwini, C., 2017. Bengal gram seed husk as an adsorbent for the removal of dye from aqueous solutions – batch studies. *Arab. J. Chem.* 10, S2554–S2566. <https://doi.org/10.1016/j.arabjc.2013.09.029>.
- Song, X., Zhang, Y., Yan, C., Jiang, W., Chang, C., 2013. The langmuir monolayer adsorption model of organic matter into effective pores in activated carbon. *J. Colloid Interface Sci.* 389, 213–219. <https://doi.org/10.1016/j.jcis.2012.08.060>.
- Speight, J.G., 2017. Transformation of inorganic chemicals in the environment. *Environmental Inorganic Chemistry for Engineers*. CD & W Incorporated, Wyoming, United States. <https://doi.org/10.1016/B978-0-12-849891-0.00007-2>. p. 363.
- Sumalinog II, M.J.R., Arazo, R.O., De Luna, M.D.G., 2012. A kinetic study on the adsorption of reactive yellow 145 (RY 145) dye onto activated carbon prepared from Theobroma cacao pods. AUNSEED (Ed.), 4th Regional Conference in Chemical Engineering. Kuala Lumpur, Malaysia.
- Tan, I.A.W., Ahmad, A.L., Hameed, B.H., 2008. Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: equilibrium, kinetic and

- thermodynamic studies. *J. Hazard. Mater.* 154, 337–346. <https://doi.org/10.1016/j.jhazmat.2007.10.031>.
- Tan, P., Bi, Q., Hu, Y., Fang, Z., Chen, Y., Cheng, J., 2017. Effect of the degree of oxidation and defects of graphene oxide on adsorption of Cu²⁺ from aqueous solution. *Appl. Surf. Sci.* 423, 1141–1151. <https://doi.org/10.1016/j.apsusc.2017.06.304>.
- Thuan, T., Van, T.B., Quynh, P., Duy, T., Thanh, V.T., 2016. Response surface methodology approach for optimization of Cu²⁺, Ni²⁺ and Pb²⁺ adsorption using KOH-activated carbon from banana peel. *Surf. Interfaces* 6, 209–217. <https://doi.org/10.1016/j.surfin.2016.10.007>.
- Viotti, V., Moreira, W., dos Santos, O., Bergamasco, R., Vieira, A.M., Vieira, M.F., 2019. Diclofenac removal from water by adsorption on Moringa oleifera pods and activated carbon: mechanism, kinetic and equilibrium study. *J. Clean. Prod.* 219, 809–817. <https://doi.org/10.1016/j.jclepro.2019.02.129>.
- Yurdakal, S., Garlisi, C., Levent, O., Bellardita, M., Palmisano, G., 2019. Photocatalyst characterization techniques: adsorption isotherms and BET, SEM, FTIR, UV-Vis, photoluminescence, and electrochemical characterizations. In: Marci, G., Palmisano, L. (Eds.), *Heterogeneous Photocatalysis: Relationships With Heterogeneous Catalysis and Perspectives*. Joseph P. Hayton, Palermo, Italy, pp. 87–152. <https://doi.org/10.1016/B978-0-444-64015-4.00004-3>.
- Zuorro, A., Lavecchia, R., 2012. Spent coffee grounds as a valuable source of phenolic compounds and bioenergy. *J. Clean. Prod.* 34, 49–56. <https://doi.org/10.1016/j.jclepro.2011.12.003>.