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Advanced Treatment of Pre-treated Commercial Laundry Wastewater by Adsorption Process: Experimental Design and Cost Evaluation

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ABSTRACT
In Turkey, the commercial laundry wastewater is usually discharged to the receiving water bodies and its reuse potential is ignored. This wastewater is grouped into the greywater due to their content of organic and inorganic pollutants. In recent years, the sequential processes have become more preferable in greywater treatment and reuse. In this study, a batch adsorption process was applied for further treatment of commercial laundry wastewater which is also pre-treated by means of the electrocoagulation process. In adsorption, two different composites of waste hazelnut shell derived activated carbons, which are supported with polyaniline (PAn/HS) and polypyrrole (PPy/HS), were used as adsorbents. The efficiency of the process was evaluated by means of an experimental design, and the response surface methodology was applied for this purpose. In the experiment with PAn/HS, the chemical oxygen demand (COD) 75% removal efficiency was accomplished with adsorbent dosage of 0.9 g, at pH 8, with 125 rpm mixing rate and for 77.5 min reaction time. For PPy/HS under the same experimental conditions, the COD removal efficiency was obtained as 20%. The utilization of waste hazelnut shell derived composites as adsorbents for commercial laundry wastewater treatment is a good alternative. The production costs of adsorbents were estimated as 0.70 USD/g and 3.21 USD/g for PAn/HS and PPy/HS, respectively. In terms of the production cost, the PAn/HS composite is approved more agreeable as adsorbents for commercial laundry wastewater treatment.

Keywords: adsorbent synthesis, COD removal, experimental design, laundry wastewater, polymer supported composites

INTRODUCTION

Commercial laundries are one of the service industries which use high amounts of water and consequently produce high load of wastewater. The wastewater of this industry is accepted as greywater [Braga and Varesche 2014] and usually available for reuse, despite its high surfactant content and other organic/inorganic contaminants [Tripathi et al. 2013]. The variation of these pollutant parameters in this wastewater may change according to the items washed and the compounds used for cleaning purposes such as detergents, bleachers, softeners, etc. For eliminating or reducing these pollutants several processes are applied in order to treat or reuse the laundry wastewater, such as biological processes [Bering et al. 2018; Delforno et al. 2015], physicochemical processes [Adesoye et al. 2014; Mohan 2014; Kaleta and Elektorowicz 2013], filtration [Korzenowski et al. 2012] and adsorption [Schouten et al. 2009; Pal et al. 2013]. Among these processes, adsorption is a feasible and relatively economic method for the treatment of laundry wastewater [Ciabattia et al. 2009; Tsyntsarski et al. 2014].

Low-cost waste precursors such as walnut [Nazari et al. 2016] or hazelnut shells [Pehlivan et al. 2009], sunflower seed hulls [Zou et al.

2015], sawdust [Foo and Hameed 2012a], fruit peels [Foo and Hameed 2012b], etc. may be used for activated carbon production and they become good adsorbents for the reduction of COD or other pollutants in wastewaters. Additionally, polymers such as polyaniline and polypyrrole are used as a modification compound to enhance the sorption features of some materials [Ayad and El-Nasr 2010; Ghorbani et al. 2010; Bhaumik et al. 2013].

The objective of this study was to investigate the adsorption of electrocoagulated laundry wastewater via PAn/HS and PPy/HS composites in terms of the COD removal efficiencies by employing Box Behnken Design (BBD) of Response Surface Methodology (RSM) and compare the composites in the economical aspect with cost evaluation.

MATERIAL AND METHODS

Preparation of the adsorbents

The hazelnut shells were obtained as household organic waste. The shells were washed with distilled water, dried in the oven (NUVE FN500) at 105°C and fractured at a particle size of 1–2 mm in a commercial coffee grinder. Activation was carried out with 100 mL of 50% H_3PO_4 solution and 50 g of the waste shell at an impregnation ratio of 1:2. Drying was applied after activation for 12 hours at 105 °C in the oven. Activated shells were carbonized for 60 min at 600°C in the furnace (PROTHERM Chamber Laboratory Furnace) under nitrogen gas (300 mL/min N_2 gas flow). After carbonization, the aniline and pyrrole monomers were polymerized.

For the polyaniline synthesis; 1 g $K_2S_2O_8$ and 100 mL (1M) H_2SO_4 solution was mixed on a magnetic stirrer and 1 g of hazelnut shell activated carbon and 1 mL of aniline monomer were added. In the ultrasonic bath (WiseClean WUC-A06H), the reaction was carried out at room temperature for 5 hours. The synthesized composites were filtered and washed several times with distilled water. It was dried for 24 hours at 60°C in the oven and cooled in a desiccator, then stored in sample containers.

For the polypyrrole synthesis; 5 g $FeCl_3$ and 100 mL distilled water was mixed on a magnetic stirrer and 1 g of hazelnut shell activated carbon and 1 mL of pyrrole monomer were added. Afterwards, the same procedure was followed then in the polyaniline synthesis.

Batch adsorption studies

The study was carried out as a batch process with 100 mL of wastewater which was obtained after the electrocoagulation process. After electrocoagulation, the COD content of the influent for adsorption process was varied between 220–280 mg/L. The effects of pH (4–12), reaction time (5–150 min), adsorbent amount (0.3–1.5 g) and mixing rate (50–200 rpm) on the COD removal efficiencies were investigated for both composites (Table 1). The experimental design was applied by using response surface methodology to determine the effects of these independent variables and also the optimum conditions. The COD analyses were performed according to standard methods.

Experimental design

BBD is a responce surface methodology (RSM) used to predict second-order models. BBD should be used when it is desired to determine the optimum conditions by obtaining mathematical expressions for the variable. For the dependent and independent variables correlation, the second order equation response was used:

$$\begin{aligned} Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + \\ +b_4X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + \\ +b_{44}X_4^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + \\ +b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + \\ +b_{34}X_3X_4 \end{aligned} \quad (1)$$

where: Y is a response variable of removal efficiency,
b_0 is constant,
b_1, b_2, b_3 and b_4 are linear coefficients,
b_{11}, b_{22}, b_{33} and b_{44} are quadratic coefficients and
b_{12}, b_{13}, b_{14}, b_{23}, b_{24} and b_{34} are cross product coefficients; x_i is coded experimental levels of the variables pH (X_1), reaction time (X_2), adsorbent amount (X_3) and mixing rate (X_4) is represented in terms of coded factors (−1, 0 and +1).

The effect of the independently expressed variables on the dependent variables was investigated in analysis of variance (ANOVA) and it was used in the mathematical model in Eq. (1). The model terms were evaluated with P-value

Table 1. Box-Behnken design matrix of independent and dependent variables

Experiment number	pH (X_1)	Reaction Time (min) (X_2)	Adsorbent amount (g) (X_3)	Mixing rate (rpm) (X_4)	COD removal efficiency (%)	
					PAn/HS	PPy/HS
1	8	5	0.9	50	41	12
2	4	77.5	1.5	125	49	22
3	4	150	0.9	125	26	32
4	8	150	0.9	50	57	12
5	8	150	0.9	200	31	28
6	8	77.5	0.3	200	28	15
7	12	150	0.9	125	44	23
8	8	150	0.3	125	55	13
9	12	77.5	0.9	50	68	15
10	12	77.5	0.9	200	38	20
11	8	77.5	0.9	125	75	15
12	8	5	0.3	125	48	50
13	8	5	1.5	125	67	12
14	12	5	0.9	125	35	52
15	8	5	0.9	200	25	19
16	4	77.5	0.3	125	63	15
17	8	77.5	0.9	125	64	23
18	8	77.5	0.9	125	62	19
19	4	77.5	0.9	50	42	8
20	4	77.5	0.9	200	33	14
21	12	77.5	1.5	125	56	24
22	4	5	0.9	125	63	9
23	8	77.5	0.3	50	71	9
24	8	77.5	1.5	50	62	11
25	8	77.5	1.5	200	41	14
26	12	77.5	0.3	125	61	48
27	8	150	1.5	125	31	48

(probability) at the 95% confidence level. When the P-values are less than 0.05, the model and model terms are statistically significant.

In addition, the Pareto Analysis was performed to determine the percentage effectiveness of independent variables on the response value. These percentages were calculated according to the Eq. (2):

$$P_i = \left(\frac{b_i^2}{\sum_{i=1}^{n} b_i^2}\right) x\,100\,(i \neq 0) \quad (2)$$

In this equation, b_i is expressed as regression coefficient in the second order model equation.

MINITAB version 17 was used to build the experimental design with response surface methodology. Before the experimental design, the intervals of the variables were determined by preliminary studies. The experimental study intervals and the levels of the independent variables were given in Table 2.

RESULTS AND DISCUSSION

Experimental design results of COD removal by adsorption process

The results of the COD removals with the PAn/HS and PPy/HS composites are given in Table 1, the model-generated equation using Box-Behnken design for PAn/Hs and PPy/HS are as follows, respectively:

Table 2. Experimental study ranges and studied levels of independent variables

Parameter	Unit	-1	0	+1
pH (X_1)	-	4	8	12
Reaction Time (X_2)	min	5	77.5	150
Adsorbent Amount (X_3)	g/100 mL	0.3	0.9	1.5
Mixing Rate (X_4)	rpm	50	125	200

$$\boldsymbol{COD_{\frac{PAn}{HS}}\ Removal}\ (\%) = 27.4 + 4.44X_1 + 0.369X_2 + 5.5X_3 + + 0.327X_4 - 0.461X_1^2 - 0.003044X_2^2 - - 6.6X_3^2 - 0.002222X_4^2 + 0.0397X_1X_2 + + 0.94X_1X_3 - 0.0058X_1X_4 - 0.2471X_2X_3 - - 0.000460X_2X_4 + 0.1222X_3X_4 \quad (3)$$

$$\boldsymbol{COD_{\frac{PPy}{HS}}\ Removal}\ (\%) = -12.3 + 4.32X_1 - 0.286X_2 - 26.0X_3 + + 0.448X_4 + 0.242X_1^2 + 0.001403X_2^2 + + 10.42X_3^2 - 0.001644X_4^2 - 0.04483X_1X_2 - - 3.229X_1X_3 - 0.00083X_1X_4 + 0.4195X_2X_3 + + 0.000414X_2X_4 - 0.0167X_3X_4 \quad (4)$$

The calculated values according to Eq. (3) and Eq. (4) were compared with the experimental values obtained from the studies and shown in Figures 1a and 1b for PAn/HS and PPy/HS composites, respectively.

According to the results, the R-squared value corresponded to the experimental values and the calculated values for PAn/HS and PPy/HS composites were 0.82 and 0.95, respectively. This comparison showed that the built model for PPy/HS was more suitable for the evaluation of the adsorption studies with this composite.

The results of the ANOVA of the Box-Behnken design for COD removal by adsorption process were given in Table 3.

In Table 3, as ANOVA results showed that in general; all linear, square and two-way interaction models were found statistically significant (p <0.05) for evaluating the COD removal by adsorption process both with the PAn/HS and PPy/HS composites. Furthermore, the values of the R2 obtained for the reliability of the program was 93% and 95%, the predicted R2 value was 65% and 73%, the adjusted R2 value was 85% and 89% for PAn/HS and PPy/HS, respectively. According to these R2 values, reliability of the models was quite high to provide a good evaluation of the COD removal efficiencies of adsorption processes with the presented independent variables.

The contour graphs drawn according to the model created with the Box-Behnken design are given in Figure 2a-b.

According to Figure 2a, when the ''pH-reaction time'' interaction is considered, about 67% efficiency may be achieved at pH 7.8 for a run of 65 min. Above and below these pH values and reaction time, the COD removal efficiency tends to decrease. When the "pH-adsorbent amount" interaction was examined, it was determined that

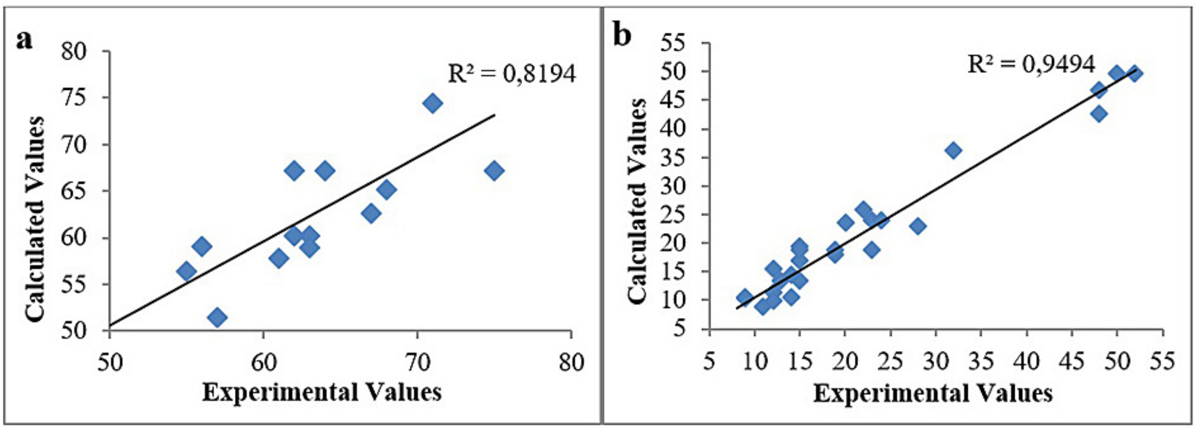

Figure 1. Comparison of experimental values with calculated values for **a)** PAn/HS and **b)** PPy/HS composites

Table 3. ANOVA table of PAn/HS and PPy/HS composites adsorption studies

		PAn/HS				PPy/HS			
Source	DF	Adj SS	Adj MS	F-value	P-value	Adj SS	Adj MS	F-value	P-value
Model	14	6043.42	431.67	11.40	0.000	4324.25	308.88	16.09	0.000
Linear	4	3046.17	761.54	20.10	0.000	744.83	186.21	9.70	0.001
Square	4	1827.50	456.88	12.06	0.000	1308.17	327.04	17.03	0.000
2-Way Interaction	6	1169.75	194.96	5.15	0.008	2271.25	378.54	19.71	0.000
Error	12	454.58	37.88			230.42	19.20		
Lack-of-Fit	10	356.58	35.66	0.73	0.703	198.42	19.84	1.24	0.526
Pure Error	2	98.00	49.00			32.00	16.00		
Total	26	6498.00				4554.67			

there would be 67% COD removal at pH 8 with a minimum 0.68 g/100 mL adsorbent amount. Considering the "pH-mixing rate" interaction, it was observed that over 70% efficiency could be achieved with 50 rpm at the pH range of 6.5–10.

The maximum removal could be achieved as 72% at pH of 8.6 with 79 rpm according to the model. When the ''reaction time-adsorbent amount'' interaction was evaluated, it was determined that 67% of COD removal efficiency could be reached with 0.88 g/100 mL adsorbent amount for 67 min. According to the interaction between "reaction time-mixing rate", when the system is run for 80 rpm for 70 min, a COD removal efficiency of 72% may be achievable. When the "adsorbent amount-mixing rate" interaction was examined, the minimum adsorbent amount could be 0.3 g/100 mL for 75% of COD efficiency with mixing rate of 63.5 rpm. This value was also the highest that was obtained from the experimental studies with PAn/HS composite.

In Figure 2b, the 2-way interaction graphs showed that the COD removal efficiencies of the PPy/HS were lower in comparison with PAn/HS. According to the graphs, the highest achievable efficiency may be 50% when 0.3 g/100 mL adsorbent is applied for 5 min.

With the calculations performed according to Eq. (2), the most effective factor in the removal of COD by PAn/HS adsorption was found to be the adsorbent amount with 77.74% and also pH with 20.99% as secondary active factor. For PPy/HS, the adsorbent amount was also the most effective factor with 96.36%. According to the Table 1, the highest COD removal efficiency was obtained in the 11th run as 75% for PAn/HS composite. In comparison with this study, a similar COD removal efficiency (70.12%) was achieved by a chemical coagulation-flocculation/ultraviolet photolysis with the same initial COD concentration of a laundry wastewater [Terechova et al. 2014]. On the other hand, the COD removal efficiencies are low for PPy/HS when compared with PAn/HS and the highest achieved COD removal was only 52% in the 14th run.

Cost evaluation

In order to understand the economic framework of the adsorbent synthesis for laundry wastewater treatment, the cost evaluation was performed according to the step by step calculations. From the preparation of the raw shells to the activated carbon production and then the synthesis of composites, all cost items were considered such as water, energy, chemicals consumption and other equipment utilization. According to these items, the costs for 1 g of composite synthesis were 0.70 USD and 3.21 USD for PAn/HS and PPy/HS, respectively.

CONCLUSIONS

The adsorption studies with PAn/HS and PPy/HS composites to treat laundry wastewater were conducted and the highest COD removal efficiencies were achieved as 75% and 52%, respectively. The studies were conducted according to an experimental BDD and models were built to understand the nature of COD removal by adsorption process with the synthesized composites via considering pH, time, adsorbent amount and mixing rate as operational parameters. The built models were quite representative when the experimental and calculated efficiencies were compared. Additionally, the Pareto analysis was applied and the most effective factor was obtained as the adsorbent amount for both composites.

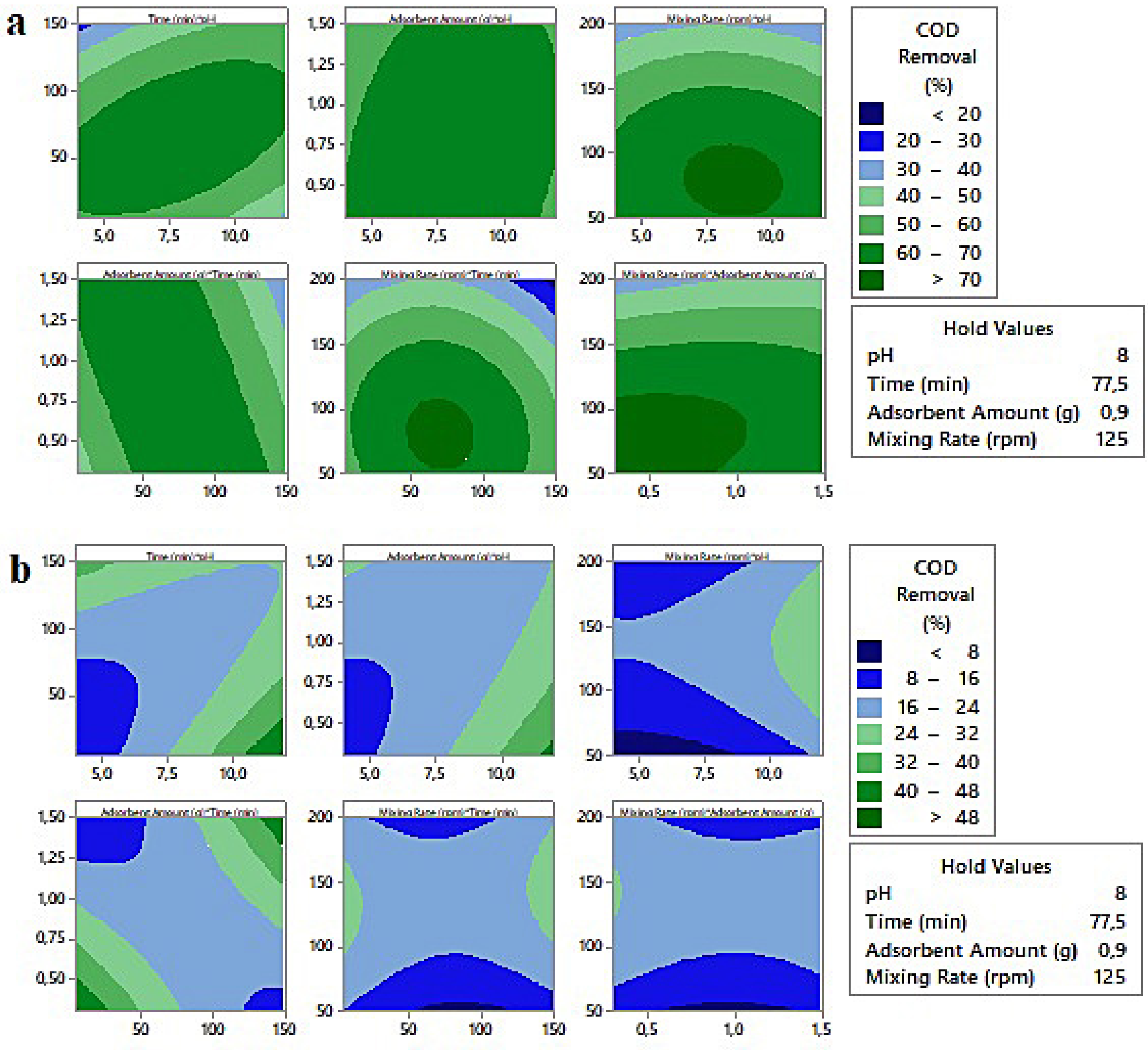

Figure 2. Contour plots for COD removals of **a)** PAn/HS and **b)** PPy/HS

As a result, it was determined that PAn/HS can be a more suitable adsorbent for the removal of COD from laundry wastewater in comparison with PPy/HS from both experimental and economical aspects. Further investigations with alternative operational parameters or other levels of parameters chosen in this study should be conducted to understand the potential of this material as adsorbent in a wide perspective.

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