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Research Article

Treatment of Barber Salon Greywater by Adsorption Process: Comparison of Activated Carbon, Human Hair, and Basalt

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Abstract

Personal care products (PCP's) are products used commonly to maintain personal hygiene. It has been found that PCP's are affecting the water bodies over the world. Conventional treatment methods are not sufficient for the treatment of PCPs. In this study, the removal of PCP's from barber salon wastewater - greywater by the adsorption process was investigated. The effects of the adsorption process on chemical oxygen demand (COD) by different adsorbents; activated carbon, raw human hair, and basalt were assessed and compared. For this aim, 1 g of the adsorbents were added into 100 mL of the greywater of barber salon. Mixtures were added into 250 mL beaker to prevent any unpredicted loss. The beakers were agitated at 150 rpm in an orbital shaker for 24 h at room temperature. The initial value of the COD was measured as 2400 mg/L. The COD removal efficiencies by activated carbon, raw human hair, and basalt adsorption were founded to be 63.0%, 85.0%, and 38.3% respectively. Since the maximum removal efficiency was obtained when basalt was used as an adsorbent, the response surface method was used to design and optimize the adsorption process onto the basalt only. The adsorption capacity increased until the 40th minute when the adsorbent dosage was 0.228 g, then the capacity had been constant at 721 mg/g. The results were fitted with Freundlich isotherm. And the adsorption kinetics was fitted to Pseudo second-order.

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BERBER SALONU GRI ATIK SUYUNUN ADSORPSIYON PROSESI ILE ARITIMI: AKTIF KARBON, INSAN SAÇI VE BAZALT ADSORBENTLERININ KARŞILAŞTIRILMASI

Özet

Kişisel bakım ürünleri (PCP), kişisel hijyeni korumak için yaygın olarak kullanılan ürünlerdir. PCP'lerin dünyadaki su kaynaklarını etkilediği daha önceki çalışmalarda bulunmuştur. Geleneksel arıtım yöntemleri ise PCP içeren atık suların arıtımı için tek başına yeterli değildir. Bu çalışmada, PCP içeren berber salonundan alınan gri atık suyun adsorpsiyon işlemi ile arıtımı araştırıldı. Adsorpsiyon işleminin farklı adsorbanlar (aktif karbon, ham insan saçı ve bazalt) tarafından, kimyasal oksijen ihtiyacı (COD) üzerindeki etkisi değerlendirildi ve karşılaştırıldı. Bu amaçla, 100 mL berber salonunun gri suyuna 1 g adsorban ilave edildi. Deneyler sırasında beklenmedik bir taşmayı önlemek için 250 mL'lik behere karışımlar ilave edildi. Beherler, oda sıcaklığında 24 saat boyunca bir orbital çalkalayıcıda 150 rpm'de çalkalandı. Atık suyun, KOİ'nin başlangıç değeri 2400 mg/L olarak ölçüldü. Aktif karbon, ham insan saçı ve bazalt adsorpsiyonu ile KOİ giderim verimi sırasıyla; %63.0, %5.0 ve %38.3 olarak tespit edildi. Yanıt yüzeyi yöntemi (RSM), sadece maksimum giderim verimliliği elde edilen bazalt adsorbanı için, adsorpsiyon işlemini tasarlama ve optimize etme için kullanıldı. Adsorpsiyon kapasitesi, adsorbent miktarı 0.228 g olduğunda 40. dakikaya kadar arttı, daha sonra kapasite 721 mg/g'da sabitlendi. Sonuç olarak adsorpsiyon işlemi; Freundlich izotermi ve Pseudo ikinci dereceden kinetik reaksiyonuna sahip olduğu bulundu.

Anahtar Kelimeler
Berber salonu gri suyu
Bazalt
Adsorpsiyon
Tepki yüzeyi yöntemi

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INTRODUCTION

In recent years, human life standard had been improved as a result of the development of civilization. Many materials have been produced to keep up with this development. One of these products is personal care products (PCP's). PCP's are the product aiming to maintain personal hygiene [1, 2]. It can be found as neutral, anionic, cationic or zwitterion [3]. Since the 1990s, the PCP's have been acknowledged as an emerging contaminant. PCPs can be discharged to the environment through human excretion, treatment plants, and industrial facilities [4, 5].

Conventional wastewater treatment plants were established to treat urban wastewaters. However, as PCP's usage has increased in recent years, its concentration in sewage water has increased. Previous studies showed that PCP is present in the effluent of treatment plants [6]. This shows that conventional purification methods are not sufficient for the treatment of PCPs [6, 7]. Previous studies have explored the presence of PCP's in water bodies and have founded more than 100 types of PCP's [8, 9].

Many researchers have employed different treatments techniques to remove PCP's from water. Researchers have noticed a fluctuation in the PCP's removal efficiency by activated sludge systems because several types of PCP's are antimicrobial agents [10]. Many researchers have investigated the electrochemical process. They have reported a high efficiency for the degradation of PCP's [11, 12, and 13]. The main problem in this type of treatment is the possibility of production of bio-recalcitrant by-products [14]. Membranes have also shown efficacy in treated of PCP's [15, 16]. The membranes efficiency depend on the diameter and the molecular weight of the PCP's, which are vary from one to another [17].

The using of the adsorption process to remove the PCP's was extensively investigated. The adsorption process is a simple, flexible, and economic beneficiary [18, 19]. These features made the process more favorable. The limitation in this technique is the disposal/ regeneration of the adsorbent, which can be considered as second-order contamination [20].

Activated carbon can be considered the most common adsorbent. The relatively high cost of it led the researchers to find low-cost adsorbent [21]. Agricultural solid wastes [22], industrial by-products [23], clay minerals [24, 25], and montmorillonite [26] are some of the examples of the low-cost adsorbents which were employed to remove PCP's from liquids.

Ma and Chen (2018) stated that the many components in the cosmetic products comprised of glycerol or ethanol, fatty acids, and fatty alcohols. At the result of the presence of these components, The COD concentration was noticed to range from 45650-5900 mg/L [27]. PCP is a major part of COD in real barber wastewater [28]. In this study, a commercial activated carbon was used to treat the wastewater discharged from the barber salons. Human hair as a bio-sorbent and basalt as an industrial by-product were used as a low-cost alternative. The chemical oxygen demand (COD) removal efficiencies were recorded and compared with others. The adsorbent with the maximum removal efficiency was modeled and optimized by response surface method.

MATERIAL AND METHOD

Material

In this study, the greywater generated from barber salons was treated by different low cost adsorbents (raw clean human hair and basalt). The efficiencies of COD removal by these adsorbents and commercial activated carbon were compared. Raw clean human hair was collected from barber salon. Basalt was collected from industrial treatment sludge of a basalt processing plant in Osmaniye. - Commercial activated carbon was also used for experiments.

Men’s barber salon load calculation

The number of barber salons in Mersin was obtained from the relative agencies. Water bill samples were collected from barber salons to estimate the monthly consumption. The chemical oxygen demand was measured by Closed Reflux, Titrimetric Method (5220 C) [29].

Sample collection

A tank was connected to the sanitary system of the salon to collect the sample from men’s barber salon. The tank is mounted on the outlet of the barber basin to avoid mixing with the black water. It was taken into consideration that the wastewater had been generated by the different hair treatment process.

Batch studies

In the batch studies, the removal of COD by human hair, basalt, and active carbon was assessed. The initial and final COD was measured. To achieve that, the method in the previous work [30] was used with some modifications, 1 g of the adsorbent were added into 100 mL of the greywater of barber salon. Mixture were added into 250 mL beaker to prevent any unpredicted loss. The beakers were agitated at 150 rpm in an orbital shaker for 24 h at room temperature. The efficiencies of the COD removal were calculated by Eq. (1).

$$COD\ removal\ \% = \frac{COD\ i - COD\ f}{COD\ i} \times 100\% \quad (1)$$

The adsorption capacity (mg.g^{-1}) for each adsorbent was identified separately as shown in Eq. (2).

$$Adsorption\ Capacity = \frac{(COD\ i - COD\ f) \times V}{M} \quad (2)$$

Where COD_i and COD_f are the initial and final COD respectively (mg.L^{-1}); V is the volume of the solution (L); M adsorbent mass (g).

The material that had the maximum COD removal was optimized by Response surface Method.
The Freundlich [31] and Langmuir [32] models was used to study the adsorption isotherms as shown in Eq. (3) and Eq. (4) respectively:

$$Log(q_e) = Log(K_L) + (\frac{1}{n}) \times Log(C_e) \quad (3)$$

$$\frac{C_e}{q_e} = \frac{a_L C_e}{K_L} + \frac{1}{K_L} \quad (4)$$

Where K_L is the energy of the adsorption (L mg^{-1}); n is the factor of heterogeneity; and a_l is the Langmuir constants (L.mg^{-1}).

Adsorption kinetics

The change of COD concentration over time was measured. The process continued until the COD concentration of the samples became closer. Lagergren's pseudo first order model and pseudo second-order model were used to describe the adsorption kinetics as shown in Equations (5) and (6) respectively [33, 34].

$$Log(q_e - q_t) = Log q_e - (k1/2.303)t \quad (5)$$

$$t/q_t = 1/(K_2 q_e^2) + (1/q_e)t \quad (6)$$

Response surface method

The COD removal efficiency was modeled by Response surface Method (RSM). Contact time and adsorbent dosage were represented using a Central Composite Design (CCD). The experimental replicates necessary to build the model were calculated using Eq. (7).

$$N = 2^n + 2n + Cp \quad (7)$$

Where N, n, Cp is the experimental runs, independent factor, and center point replicates, respectively.
The modeling process was established using Design expert v11 program. 13 experiments were accomplished.

RESULT AND DISCUSSION

Hydraulic load of Men's barber salon wastewater in Mersin

Hydraulic load of men's barber salon wastewater in Mersin city, Turkey was calculated. The research findings showed that Mersin city has 1119 men's salons and 1081 women's salon at the city center. This study focused on the men's barber salons. Therefore, the result in Table 1 belongs to the men's salons only.

Table 1. Men's barber salon wastewater loading data.

	Value	Unit
COD For men's barber salon wastewater	2400 .0	mg/L
Monthly Average water consumption	9.0	m^3
Monthly Average wastewater discharging	7.2	m^3
Daily COD loading for each salon	0.6	Kg/d
Daily COD loading for Men's Barber salons	644.5	Kg/d

Batch studies

Commercial activated carbon was compared with the low-cost adsorbent (raw human hair and basalt). All of the experiments were conducted in the same conditions (1g adsorbent, 24 h, 100 mL) at room temperature. At the end of the process, the changes in COD value were determined as shown in Table 2.

Table 2. COD changes and removal efficiency

	COD (mg/L)	Removal Efficiency (%)	Capacity (mg/g)
Men's barber salon wastewater	2400	-	-
Activated carbon	888	63.0	151.2
Basalt	360	85.0	721.0
Raw human hair	1480	38.3	92

As shown in Table 2 the maximum COD removal efficiency obtained when basalt was used as an adsorbent with a removal efficiency of 85%. The use of commercial activated carbon had decreased the COD to 888 with a removal efficiency of 63%. Mestre et al (2007) have examined the removal efficiency for ibuprofen using activated carbon. They have reported that the removal efficiency of ibuprofen exceeded 90% at pH levels from 2-4. They have also noticed that a decrease in efficiency at higher pH values [35]. Raw human hair had decreased the COD to 1480 mg/L. Saleh et al (2019) have obtained similar results [28].

Response surface method

The men's barber greywater treatment process by basalt was optimized by RSM. Basalt dosage and time changed to reach the proposed efficiency and optimum capacities were modeled by Central Composite Design. The carried experiments and the results are shown in Table 3.

Table 3. Experiments Design and the result of each run

Run	Mass (g)	Time (min)	Eff. (%)	Capacity (mg/g)
1.00	0.55	30.00	76.67	334.56
2.00	0.23	11.97	43.33	448.62
3.00	1.00	30.00	83.33	199.99
4.00	0.87	11.97	71.00	196.27
5.00	0.55	30.00	76.67	334.56
6.00	0.10	30.00	46.67	1120.08
7.00	0.55	30.00	76.67	334.56
8.00	0.55	30.00	76.67	334.56
9.00	0.55	30.00	76.68	334.60
10.00	0.55	4.50	41.00	178.91
11.00	0.55	55.50	80.00	349.09
12.00	0.23	48.03	60.00	621.22
13.00	0.87	48.03	88.00	243.26

Based on the correlation coefficient (R^2 = 0.9632), the developed model was suggested to be Quadratic. The difference between the predicted R^2 (0.8473) and the Adjusted R^2 (0.9632) was less than 0.2. This difference indicates the significance of the model. Adequate Precision measures the signal to noise ratio. The model ratio was 27.039 which is larger than 4. This ratio indicates an adequate signal and the model can be used to navigate the design space.

Analysis of variance for the developed model was used to study the significance of the model. The model was found to be significant since F-value was 63.82 (p-value < 0.0001). The model terms with P- values less than 0.05 are significant, while values greater than 0.1000 indicate the model terms are not significant. According to Table 4, the terms A, B, A^2, and B^2 are significant.

Table 4. ANOVA test for the developed model.

Source	Sum of squares	df	Mean	F-value	p-value	
Model	0.000874	5	0.000175	63.81528	1.09688E-05	Significant
A-mass	0.000672	1	0.000672	245.1843	1.04835E-06	Significant
B-time	9.47E-05	1	9.47E-05	34.57316	0.000611782	Significant
AB	4.45E-07	1	4.45E-07	0.16242	0.698963512	
A^2	4.29E-05	1	4.29E-05	15.65786	0.005482661	Significant
B^2	5.04E-05	1	5.04E-05	18.40406	0.00361071	Significant

The effects of time and basalt dosage on the treatment capacity were identified (Figure 1). The capacity of the modeled data increased with time until 40 minute. After 40 minute the capacity became constant as 721 mg/g. The mass of basalt had an inverse relationship with the capacity. The maximum capacity was 775 mg/g at 0.23 g dosage while the minimum capacity was 230.5 mg/g at 0.87 g dosage.
The capacity curve at low dose of adsorbent was clearer than the high dose. This means that the capacity at low dose had changed with time more than in high dose. The generated data from the developed model consists with the mass transfer concepts. The capacity will change for the low dosages more than the high dosages when the concentration and volume are constant.

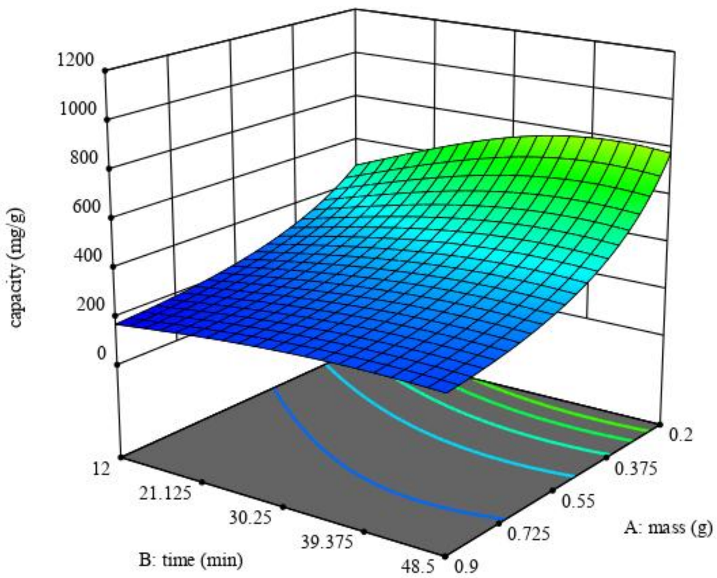

Figure 1. Mass and time effects on the capacity.

As shown in Figure 1, the relationship among the time dosage of basalt and the adsorption capacity of the basalt were also graphed. The removal of COD by basalt can be predicted at any time and any dosage. The relationship among the time, dosage of basalt, and the adsorption capacity can be mathematically written as shown in Eq. (8).

$$\frac{1}{sqrt(capacity+100)} = 0.038849213183452 + 0.054031129568089(mass) - 0.00071962712205573(time) + 0.000058131274461904(mass * time) - 0.024525525581604(mass)^2 + 0.0000082804447702283(time)^2 \qquad (8)$$

Adsorption isotherms

In this study, the adsorption mechanism was described by Langmuir and Freundlich's isotherms. The isotherms linear equations were plotted to obtain the isotherms constants. The slope and intercept were determined and summarized in Table 5.

Table 5. Isotherms parameters.

Isotherm	Parameter	Unit	Value
Freundlich	N	-	0.8331
	K_F	$L.mg^{-1}$	0.2470
	R^2	-	0.9542
Langmuir	K_L	$L.mg^{-1}$	0.6853
	a_L	$L.mg^{-1}$	0.0004
	R^2	-	0.4534

Regression coefficients R for Freundlich was higher than both Langmuir. Because of that, the Freundlich's isotherm was selected to present the adsorption process. Freundlich's isotherm suggests that the adsorbent surface is heterogonous, the adsorption process can occur in a multilayer. The plots for Freundlich and Langmuir's isotherms are shown in Figures 2 and 3 respectively.

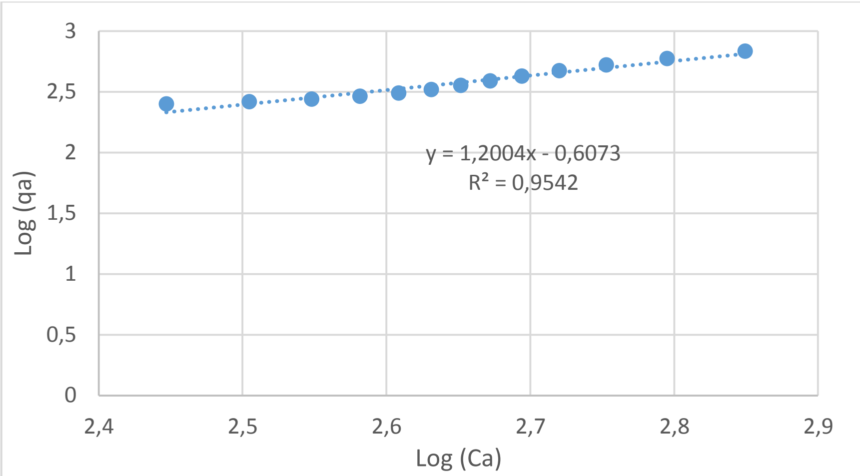

Figure 2. Freundlich's isotherm.

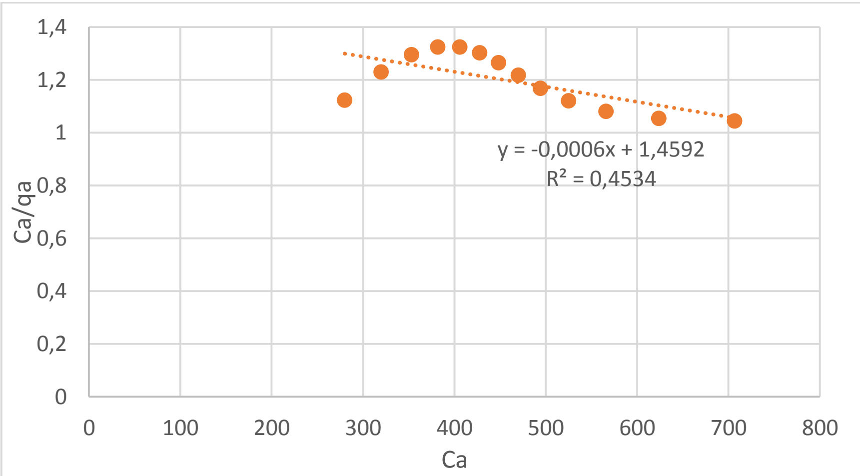

Figure 3. Langmuir's isotherm.

Adsorption kinetics

The removal of COD was assumed to follow Lagergren's pseudo first order model or pseudo second-order model. The linearity of each model was plotted and shown in Figures 4 and 5 respectively.

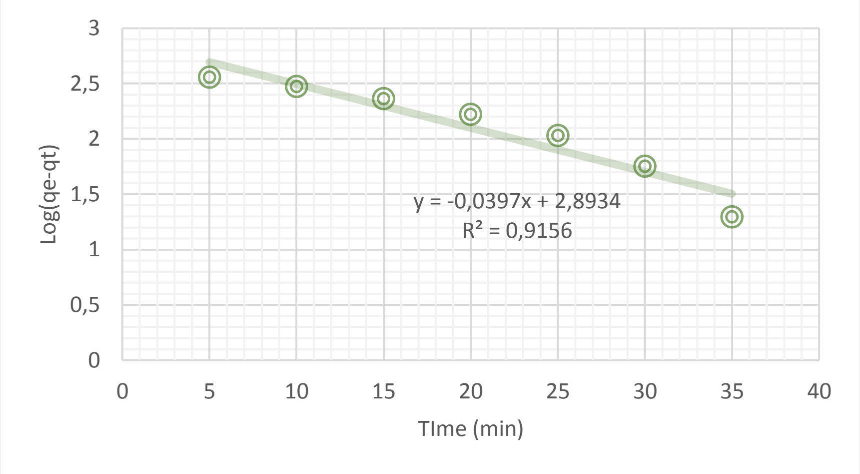

Figure 4. Lagergren's pseudo first order.

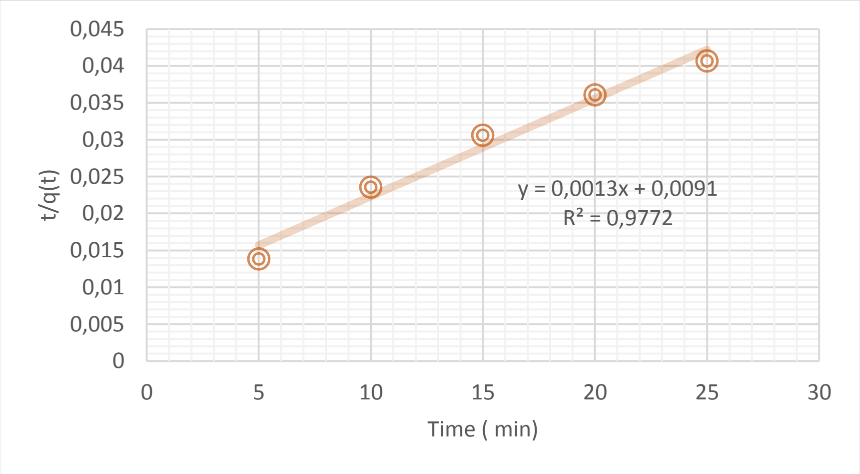

Figure 5. Pseudo second-order model.

The correlation coefficient of the Lagergren's pseudo first order model was 0.9156 is lower than the correlation coefficient for Pseudo second-order model (0.9772). Based on that, the removal of COD was fitted to pseudo second order model.

Comparison with other studies

The removal of PCP's by the adsorption process have been used widely. Manzoli et al. (2020) study the removal of cosmetics wastewater by Fenton process followed by an adsorption process. In the adsorption process a commercial activated carbon was used. The reduction in COD after the adsorption process reached 37% [34]. Table 6 shows a comparison between this study and other researches.

Table 6. Comparison with other researches.

Adsorbent	Adsorption capacity (mg/g)	Isotherm	Kinetics	Reference
Basalt	721	Freundlich	Pseudo second-order	This study
Granular Activated Carbon	323	Langmuir	-	[35]
Sulfonic acid (–SO_3H) functionalized covalent organic framework (COF-SO_3H)	770	Langmuir	pseudo-second-order	[36]
Metal organic Framework : MIL-101 (Cr)	357	Langmuir	pseudo-second-order	[37]

CONCLUSION

Men's barber salon greywater is one of the most important sources of PCPs. While the chemical oxygen demand in conventional domestic wastewater is 800 mg / L, the COD value of the greywater from the barber salons was determined as 2400 mg / L.

In this study, greywater was treated by the adsorption method to decrease COD value. Activated carbon, human hair, and basalt were used as low-cost adsorbents. The best yield was obtained from the process where basalt was used as the removal efficiency reached 58%. The adsorption capacity reached 721 mg/g. The results were fitted to the Freundlich isotherm. The adsorption kinetics was fitted to pseudo-second-order.

Basalt was collected from the industrial treatment sludge of a basalt processing plant. The use of waste materials as low-cost adsorbents is an example of green engineering practice. As a result, it was found that basalt can be used effectively in the treatment of barber greywater by adsorption. This work can be considered as an exploratory study for using basalt as an adsorbent for barber greywater. A pilot study should be accomplished to realize the work. Also, various researches should be accomplished to study the reusing of basalt after the adsorption process.

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