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REMOVAL OF REACTIVE DYE REMAZOL BRILLIANT BLUE R FROM AQUEOUS SOLUTIONS BY USING ANAEROBICALLY DIGESTED SEWAGE SLUDGE BASED ADSORBENTS

Article Highlights

- Adsorbents were produced via thermal and chemical activation processes
- Adsorption studies were conducted in batch equilibrium conditions for different dye concentrations
- Chemically activated sewage sludge indicated better porous structure
- Adsorption process demonstrated better compliance with pseudo-second order kinetic model
- Freundlich isotherm provided better fit to the equilibrium data for all adsorbents

Abstract

In this study, adsorbents were produced from sewage sludge via chemical and thermal activation processes. Experiments were carried out in a tubular furnace at a heating rate of 20 °C min⁻¹ and temperature of 550 °C with a nitrogen flow rate of 400 mL min⁻¹ for 1 h. Dye adsorption experiments were performed with Remazol Brilliant Blue R at several concentrations under batch equilibrium conditions by comparing sewage sludge based adsorbents with raw material and a commercial activated carbon. Maximum adsorption capacities of carbonized sewage sludge (CSWS) and activated sewage sludge (ASWS) were found as 7.413 and 9.376 mg g⁻¹ for 100 mg L⁻¹ dye solution, whereas commercial activated carbon had a capacity of 11.561 mg g⁻¹. Freundlich and Langmuir isotherms were used to explain the adsorption mechanism together with pseudo-first-order and pseudo-second-order kinetic models. The Langmuir isotherm, which had adsorption capacities of 34.60 (CSWS) and 72.99 mg g⁻¹ (ASWS), provided a better fit to the equilibrium data than that of the Freundlich isotherm. The pseudo second-order model, which had adsorption capacities of 7.451 (CSWS) and 9.319 mg g⁻¹ (ASWS), was very favorable to explain the adsorption kinetics of the dye with high regression coefficients.

Keywords: sewage sludge, carbonization, activated carbon, adsorption, Remazol Brilliant Blue R.

Synthetic dyes frequently cause pollution problems when the colored wastewater is discharged into surface waters after its applications. Because of their resistance to conventional wastewater treatment processes, brightly colored water-soluble reactive and acid dyes are among the most problematic dyestuff

[1]. Problems of synthetic dyes pollution have arisen day by day since they are extensively used due to their easy application techniques, inexpensive synthesis costs, low energy consumption and variety of color compared with natural dyes [2]. Furthermore, synthetic dyes are not easily biodegradable; therefore, after broad treatment applications colors may still stay in the wastewater stream. These streams are a growing threat to aquatic life because of their high chemical oxygen (CODs) and biological oxygen demands (BODs), toxic, allergic, skin irritating, mutagenic and carcinogenic features [3-6]. Because of these

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problems, many investigations on the removal of dye color from industrial effluents have appeared in recent years effective physical and chemical treatment methods including adsorption, chemical coagulation, precipitation, ultra-filtration, electro-dialysis, ionizing radiation, ozone oxidation and photo-catalytic degradation for the treatment of dye containing wastewater streams [2,7-9]. Moreover, biological materials such as algae, fungi, bacteria and yeast have been alternatively used for the removal of dyestuff from wastewater [10]. Among all these methods, adsorption process was considered excellent as compared to other techniques for its easy design and operation, effectiveness and high efficiency [11,12].

Previous research studies have used several different adsorbents like carbon nanotubes (CNTs) for dye uptake from wastewater environments [13-15]. Among these adsorbents, activated carbon was found to achieve great performance in the adsorption of various pollutants, not only at the laboratory scale, but also for industrial applications [16-18]. However, despite these excellent properties, utilization of commercial activated carbon is sometimes restricted due to relatively expensive starting material and therefore higher application costs. Furthermore, after a few uses of the original activated carbon, a saturation phenomenon occurs on the active surface sites and subsequently the activated carbon cannot no longer adsorb the adsorbates from the wastewater due to diffusion limitations. Once the activated carbon is saturated, a regeneration step is required for further treatment applications [19-21].

Attempts have been made to produce low-cost carbon-based adsorbents from alternative feedstock such as agricultural [22-24], industrial byproducts or waste [25-28], such as sewage sludge that may be a substitute for commercial activated carbons in the adsorption of various pollutants in wastewater treatment applications. Agricultural waste and industrial byproducts are very important feedstock for the manufacture of activated carbon since they are abundant, renewable, easy available and sustainable alternative sources.

Sewage sludge is a waste material produced as a byproduct of wastewater purification processes in urban and industrial wastewater treatment plants. Nowadays, its production is rapidly increasing and will continue to rise, because more municipal wastewater will be treated due to environmental necessity and legal requirements to reach better standards for wastewater treatment along with the urbanization and industrial development [29,30]. Sewage sludge is a very complex substance consisting of biological, org-

anic and inorganic components and water. It contains undigested organic compounds remained after the treatment, which are proteins and peptides, lipids, polysaccharides, plant macromolecules and aliphatic structures [31].

Considering that sludge reduction is restricted due to sustainability of wastewater treatment to reach the higher standards, it will be desirable to develop innovative, eco-friendly and effective new routes for the valorization of this "waste of the waste", so it will turn into a useful feedstock [32]. Thus, various handling methods have been utilized for the sewage sludge disposal in a sustainable way. These methods can be categorized into two main strategies consisting of traditional disposal or reuse and energy applications. Until now, sewage sludge has been used as a renewable feedstock to produce energy via anaerobic digestion, combustion, gasification, pyrolysis/carbonization and novel technologies such as wet oxidation and supercritical water oxidation [33].

Among these methods, pyrolysis (carbonization) - the thermal destruction of biomass under inert atmosphere - is a clean and efficient application, and it generates valuable liquid, gas and solid products depending on the process conditions [34]. Because of carbonaceous structure, abundant organic compositions and volatile components, sewage sludge is a reasonably appropriate candidate for manufacturing porous adsorbents under controlled carbonization conditions [35]. Activated carbon production by using sewage sludge means both a considerable saving for starting material costs, and a way of making economically valuable utilization of a waste via producing a useful material. Utilization of sewage sludge for the production of activated carbon used for the advanced treatment process of wastewater reduces the operating expenses of the plant. Moreover, this strategy solves pollution, odor and space occupation problems derived from sewage sludge in the plant [33,36].

Many studies have demonstrated that the sewage sludge was a great in-expensive and easy available feedstock for the production of activated carbon [37]. These studies mainly related with the adsorption of phenol and phenolic compounds, heavy metals, pollutant gases and dyes onto sewage sludge based adsorbents [38-40]. Among these studies dye adsorption was the most commonly applied method to determine uptake capacity of these adsorbents and the methylene blue was frequently used as an adsorbate in the dye adsorption experiments [41,42].

Remazol Brilliant Blue R dye used as an adsorbate in our present study is one of the most important reactive dyes in the textile industry. It is an anthra-

quinone-based dye and represents an important class of toxic and recalcitrant organo-pollutants. Remazol Brilliant Blue R (RBBR) is frequently used as a starting material in the production of polymeric dyes [43]. So far, several attempts have been made to remove RBBR from aqueous solutions by using various adsorbents and alternative adsorption techniques. Although several studies have been reported in the literature about the RBBR adsorption on the various adsorbents produced from different feedstock and other dyes on the sewage sludge based adsorbents, there has been no research concerning the adsorption of RBBR onto adsorbents produced from sewage sludge. Thus, this study focuses on investigating the RBBR removal efficiencies of low-cost and eco-friendly adsorbents produced from sewage sludge by using chemical and thermal activation methods.

EXPERIMENTAL

Materials

Sewage sludge samples were collected from Atakoy advanced biological wastewater treatment plant, which is an urban treatment plant located in Istanbul, Turkey. The sludge had been anaerobically stabilized by means of biogas production process subsequent to activated sludge treatment. Furthermore, it was dewatered via centrifugation process and was dried by using a rotary disc drier at the plant to

an average dry solid content of 90%. Proximate analysis of sewage sludge sample was carried out according to ASTM D3172-13 (Standard Practice for Proximate Analysis of Coal and Coke). Ultimate analysis of sewage sludge sample was performed by using an ultimate analyzer (LECO, CHNS-932), following ASTM D3176 (Standard Practice for Ultimate Analysis of Coal and Coke). Finally, macro and trace element composition of sewage sludge sample was determined by the inductively coupled plasma atomic emission spectrometry, ICP-OES (Perkin-Elmer, Optima 2100 DV). The results of proximate, ultimate and elementary analyses for sewage sludge sample are shown in Table 1. Additionally, a commercial activated carbon (Analiz Kimya Co., Turkey) was used for the adsorption experiments for the comparison. Zinc chloride (reagent grade, Merck) was used in the adsorption experiments as a chemical activation reagent. A stock solution of Anthraquinone dye Remazol Brilliant Blue R (Reactive Blue 19; $C_{22}H_{16}N_2O_{11}S_3$) was used for the adsorption studies.

Preparation of the adsorbents

Before the carbonization experiments, powdered raw sewage sludge was dried at 105 °C in an oven (Binder) for 24 h. It was not ground and sieved because of its uniform particle size distribution. Thermogravimetric analysis (TGA) was performed by using TA SDT Q600. Simultaneous TGA/DSC equip-

Table 1. Proximate and ultimate analyses of sewage sludge sample along with macro and trace element concentrations

Proximate analysis ^a		Ultimate analysis ^b	
Parameter	Content, wt. %	Element	Content, wt. %
Moisture	5.14	Carbon (C)	38.97
Volatile matter	52.12	Hydrogen (H)	5.10
Fixed carbon	6.2	Nitrogen (N)	4.11
Ash	36.54	Sulphur (S)	0.81
		Oxygen (O) ^c	50.99
		HHV (MJ kg ⁻¹)	16.18
Elemental composition			
Element	Concentration ^d , mg kg ⁻¹	Element	Concentration ^d , mg kg ⁻¹
Calcium (Ca)	30187.55	Manganese (Mn)	202.66
Aluminum (Al)	9733.33	Boron (B)	71.46
Potassium (K)	9367.81	Lead (Pb)	64.96
Magnesium (Mg)	8927.82	Nickel (Ni)	45.41
Sulfur (S)	7366.66	Cobalt (Co)	35.55
Iron (Fe)	7358.18	Molybdenum (Mo)	5.84
Sodium (Na)	3259.73	Cadmium (Cd)	0.92
Zinc (Zn)	767.38	Arsenic (As)	nd ^e
Chromium (Cr)	369.55	Mercury (Hg)	nd ^e
Copper (Cu)	263.32		

^aAs received; ^bash free dry basis; ^ccalculated by difference; ^ddry base weight; ^enot detected

ment for the determination of thermal degradation properties of sewage sludge and produced adsorbents. Thermal analyses were conducted at a heating rate of $15\text{ }^{\circ}\text{C min}^{-1}$ from 20 to $1000\text{ }^{\circ}\text{C}$ with a nitrogen flow rate of 100 mL min^{-1} . Two different methods were used for the production of adsorbents. In the first method, dried sewage sludge samples were physically impregnated with ZnCl_2 by employing a mass ratio of 1:1 (ZnCl_2 to raw material) and then, samples were activated in a quartz pipe inserted into a horizontal split tubular furnace (Protherm ASP) with a nitrogen flow rate of 400 mL min^{-1} . The heating rate of the furnace was $20\text{ }^{\circ}\text{C min}^{-1}$ and the reaction was carried out at a final temperature of $550\text{ }^{\circ}\text{C}$ for 1 h. Adsorbents produced *via* this method were referred to as ASWS (activated sewage sludge) throughout the manuscript. On the other hand, in the second method dried sewage sludge was thermally activated without activation agent at the same reaction conditions. Adsorbents produced via this method were referred to as CSWS (carbonized sewage sludge) throughout the manuscript. After completion of the processes, these adsorbents were washed several times with diluted HCl solution and hot distilled water. Finally, they were dried at $105\text{ }^{\circ}\text{C}$ for 24 h in the oven. The particle size range of the obtained adsorbents was quite variable due to nonhomogeneous structure of sewage sludge powder. Therefore, it could roughly be determined that particle size was generally less than $180\text{ }\mu\text{m}$ (Mesh No. 80).

Characterization of the adsorbents

Some physical and chemical properties such as porosity, surface area and functional groups of the adsorbents were determined through various instruments. The scanning electron microscopy (SEM) micrographs of the adsorbents were obtained by using a JEOL JSM 5410 LV model equipment. Specimens were imaged at 20.0 kV with $10.0\text{ }\mu\text{m}$ in $1000\times$ time magnification. Spectroscopic analysis of the both of the raw material and adsorbents was performed by using Agilent Cary 630 ATR/FTIR (attenuated total reflectance/Fourier-transform infrared) equipment. The spectra of the samples were recorded in the wavenumber region between 4000 and 650 cm^{-1} . The Brunauer-Emmett-Teller (BET) surface analysis of the samples was determined by using Micromeritics TriStar II 320 equipment after degassing process, which was carried out at $110\text{ }^{\circ}\text{C}$ for 1 h.

Adsorption experiments

In the adsorption experiments, sewage sludge, produced adsorbents and commercial activated carbon (AC) as different adsorbents were used to rem-

ove RBBR dye from aqueous solutions in different concentrations. Firstly, RBBR was dissolved in distilled water to prepare 1000 mg L^{-1} stock solution. Then, this stock solution was diluted to obtain standard concentrations of 20, 40, 60, 80 and 100 mg L^{-1} for the adsorption experiments. The pH values of the standard solutions were adjusted to 3 in all cases with HCl/NaOH solutions. According to the following literature survey, all adsorption studies were carried out at constant acidic conditions (pH 3).

The pH of aqueous dye solution plays a significant role for the adsorption process of dye molecules. Dye adsorption is highly pH-dependent due to effect of pH on the surface binding sites of the adsorbent as well as the degree of ionization process of the dye molecule [54]. Therefore, setting up the pH of the solution is critical to obtain a suitable surface charge for the functional hydroxyl groups of adsorbent that interact with cations/anions of dye [55]. At lower pH, the reactive azo dyes such as anthraquinonic RBBR dissolves and releases colored negatively charged dye anions into aqueous solution, which will exhibit electrostatic attraction towards positively charged surfaces. Moreover, at acidic pH values some functional groups of adsorbent are also protonated. The dissociated anions of dye molecules are transferred from solution to the surface of adsorbent and adsorption occurs *via* the electrostatic interactions between the ions of negatively charged dye molecules and positively charged adsorbent surface. In case of RBBR, the adsorption must be due to the interaction of sulfonic ($-\text{SO}_3^-$) groups of dyes with -OH groups on the surface of the adsorbent [56-58].

At the first stage, an initial kinetic experiment was conducted in which the optimum adsorption time (equilibrium time) was determined by using 100 mg L^{-1} dye solution for 120 min. Amount of the adsorbed dyestuff was determined by using a UV-Vis equipment (Scinco S-3100) at 593 nm (λ_{max}) which is the maximum absorbance wavelength value of RBBR at the adsorption process. In the batch adsorption experiments, 40 mg adsorbent was thoroughly mixed with the 5 mL aqueous solution of dye in a sealed conical centrifuge tube placed into a tube rack. This rack was placed in a thermostated water bath shaker at a rolling speed of 200 rpm at a constant temperature of $25\text{ }^{\circ}\text{C}$ for 60 min (equilibrium time). At the end of the equilibrium period, the supernatant parts of the tubes were subsequently analyzed for the residual concentration of RBBR by using UV/Vis spectrophotometer. The amount of the remained RBBR was determined from the calibration curve obtained according to concentration-absorbance chart of starting standard sol-

utions. Finally, the amount (mg) of dyestuff absorbed by per unit weight (g) of the adsorbents (SWS, AC, ASWS and CSWS) was calculated via the following equation:

$$Q = \frac{(c_0 - c_e)V}{W} \quad (1)$$

where c_0 and c_e (mg L^{-1}) are the amount of initial and remaining RBBR in the solution at time of equilibrium respectively, V is the volume (L) of the solution, and W is the weight (g) of the adsorbent.

Besides, attempts were made to fit these kinetic data by employing the pseudo-first-order [59] and pseudo-second-order [60] models, as expressed by Eqs. (2) and (3), respectively:

Pseudo-first-order equation:

$$\ln(Q_e - Q_t) = \ln Q_e - (k_1 t) \quad (2)$$

Pseudo-second-order equation:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (3)$$

where Q_e and Q_t are the amounts (mg g^{-1}) of RBBR adsorbed onto the adsorbents at the equilibrium and at the time of t , respectively, while k_1 and k_2 are the kinetic rate constants for the pseudo-first-order (min^{-1}) and the pseudo-second-order ($\text{g mg}^{-1} \text{min}^{-1}$) adsorption processes, respectively.

After determination of Q values for all solutions, in order to develop the quantitative data further, the experimental data obtained for the equilibrium adsorption of RBBR onto the adsorbents were analyzed employing the Freundlich [61] and Langmuir [62] isotherms using Eqs. (4) and (5) given below:

Freundlich isotherm equation:

$$\log Q_e = \log K_F + \frac{1}{n} \log c_e \quad (4)$$

Langmuir isotherm equation:

$$\frac{1}{Q_e} = \left(\frac{1}{Q_{\max} b} \right) \left(\frac{1}{c_e} \right) + \frac{1}{Q_{\max}} \quad (5)$$

where Q_e (mg g^{-1}) and c_e (mg L^{-1}) are the equilibrium concentrations of RBBR dye in the solid and liquid phases, respectively, while K_F ($(\text{mg g}^{-1}) (\text{mg L}^{-1})^{-1/n}$) and n are the Freundlich constants related to the adsorption capacity and intensity, respectively. Similarly, Q_{\max} (mg g^{-1}) and b (L g^{-1}) are the Langmuir constants related to the adsorption capacity. The values of the all results were given as average of the three identical trials for each experiment. Uncertainties were pre-

sented as standard deviations in triplicate for each experiment in the related charts.

RESULTS AND DISCUSSION

Figure 1 and Table 2 present thermal analysis and obtained data from curves of TGA and DTG for the SWS, CSWS and ASWS samples. The graph shows the weight loss of sewage sludge in percentage based on the starting weight with the increasing pyrolysis temperature. As can be seen from Figure 1, weight loss of raw sludge and activated sewage sludge was separated into three discrete stages (start of decomposition, main decomposition and final decomposition) in the 20-1000 °C temperature range. However, carbonized sewage sludge showed different decomposition characteristics compared to the other two samples; it had a decomposition range that lacked exact boundaries, with the exception of dehydration and drying process (20-150 °C).

For the sewage sludge, the first step roughly occurred between 20-150 °C with a weight loss of 3.77%, which was caused by the evaporation of adsorbed and bound water molecules in the structure of sludge. This range was also very similar to activated and carbonized sludge; however, ASWS had a significant mass loss of 18.08% in this range, which could be attributed to high moisture adsorption capacity due to its porous structure. In the second step, a weight loss of 25.21% occurred between 170-600 °C for SWS. This important weight loss was explained due to decomposition of volatile organic components such as carbohydrates, proteins and lipids that constitutes a significant part of sewage sludge. Finally, a weight loss of 6.75% was observed at the third step between 600-760 °C. This loss was related with thermal decomposition of inorganic compounds such as ash, which is another important ingredient in the composition of sewage sludge.

When all three samples were compared in terms of residual mass, CSWS had the maximum residue of 76.52%, followed by SWS (59.45%) and ASWS (35.32%). This could indicate that after the carbonization process, the structure of the sludge became stricter, and weakly bonded chemical components were removed from structure, eventually leading to a lower mass loss in CSWS compared to the other samples. On the other hand, the chemical activation process provided loosening of the structure and this caused easy removal of the components from the sludge structure. According to the TGA results, temperature of 550 °C was determined as optimal for the production of adsorbents from sewage sludge.

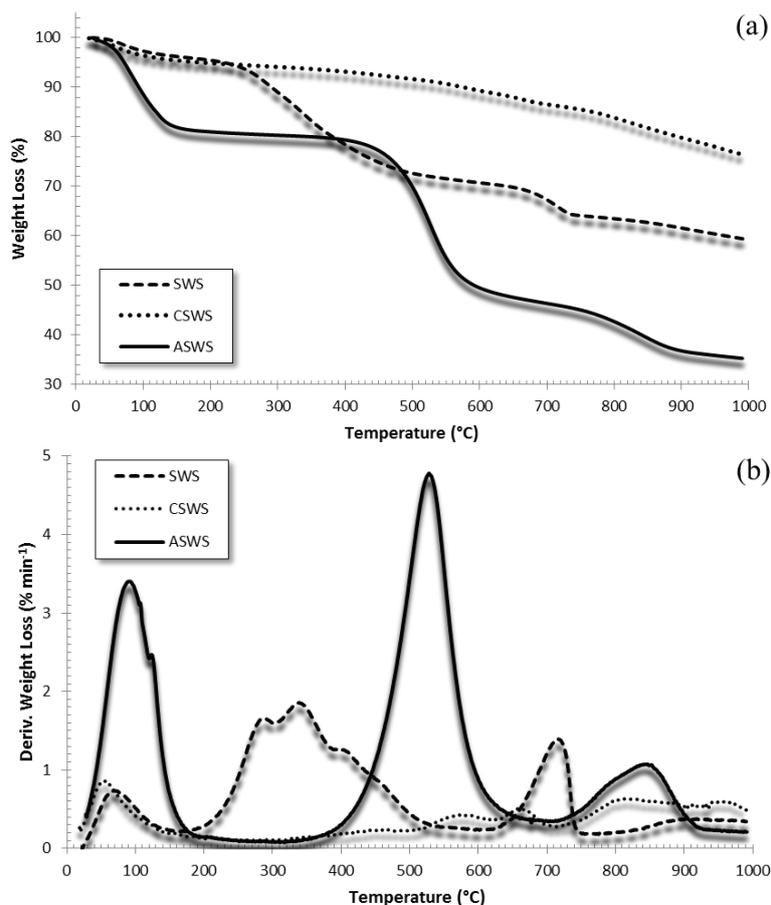


Figure 1. TGA (a) and DTG (b) curves of SWS, CSWS and ASWS.

Table 2. Characteristic parameters obtained from TGA and DTG curves for basic degradation stages

Parameter	Sample						
	SWS		CSWS			ASWS	
	DTG						
	Temperature range ^a , °C						
	170-600	600-760	340-500	500-620	620-930	320-700	700-950
$T_{\max}^b / ^\circ\text{C}$	338.95	716.38	456.35	579.63	813.89	527.26	839.71
$DTG_{\max}^c / \% \text{ min}^{-1}$	1.85	1.39	0.24	0.43	0.63	4.78	1.07
$WL^d / \%$	25.21	6.75	2.14	2.87	10.06	33.81	10.50
	TGA						
$DSP^e / ^\circ\text{C}$	170		300			320	
$HT^f / ^\circ\text{C}$	-		-			592.74	
$R^g / \%$	59.45		76.52			35.32	

^aNot included dehydration temperature range; ^btemperature of the maximum weight loss rate; ^cmaximum weight loss rate; ^dweight loss; ^etemperature of basic degradation start point; ^fhalf-life temperature; ^gresidue remained after analysis

Figure 2 shows the FT-IR spectrum of sewage sludge (SWS), carbonized sewage sludge (CSWS) and activated sewage sludge (ASWS) and commercial activated carbon (AC). As can be seen in Figure 2, SWS and CSWS are very alike with the exception of a few peaks at around 2900 and 1500 cm^{-1} , and between 650 and 800 cm^{-1} wavenumber, due to ther-

mal destruction of some chemical functional groups. The broad band between 3100 and 3600 cm^{-1} was associated with O-H stretching, which were hydroxyl-containing compounds such as water and alcohol for all samples. Moreover, it could be related with N-H stretching vibrations of amine- and amide-containing compounds.

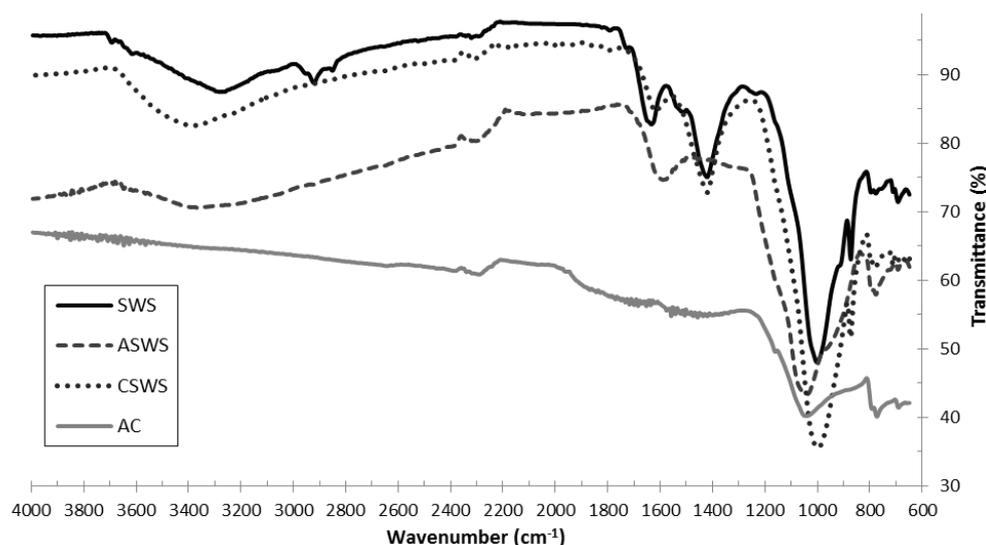


Figure 2. FT-IR spectra of SWS, CSWS, ASWS and AC.

In the spectra of SWS, the most characteristic bands at 2851 and 2922 cm^{-1} were due to stretching vibrations of aliphatic C-H bonds. These bonds could be ascribed to methylene groups and lipid compounds of SWS. These bands disappeared after thermal and chemical activation process of sewage sludge. The medium broad band at 1633 cm^{-1} related to C=O (Amide I band) stretching vibration of carbonyl groups originated from carboxylic acids and its derivatives or C=C stretching resulting from alkene compounds of SWS. It was very obvious from Figure 2 that this broad band quite shifted toward a lower wavenumber of 1620 and 1584 cm^{-1} for CSWS and ASWS, respectively. This situation could be caused by some changes in the functional groups due to thermal and chemical interactions during adsorbent production processes.

The weak absorption peak at 1520 cm^{-1} showed the presence of protein content (Amide II band) of SWS like the Amide I band. It is clear from Figure 2 that the N-H bending derived band disappeared in the spectra of CSWS and ASWS. At 1422 cm^{-1} wavenumber, medium broad band was probably caused by C-H and carboxyl O-H vibrations because of amine and hydroxyl compounds. This band completely disappeared after activation of SWS in the presence of ZnCl_2 . In the fingerprint region, the strong narrow bands between 1000 and 1100 cm^{-1} could indicate two different chemical groups. One of them was C-O stretching vibrations of alcohols and phenol compounds (aliphatic ether), and the other one was Si-O-C or Si-O-Si stretching vibrations, which related to silicon components in sewage sludge and adsorbents. Finally, for all samples the peaks in the 700-900 cm^{-1} wavenumber range in the spectra of the samples

were attributed to an aromatic C-H stretching vibration indicating the presence of adjacent aromatic hydrogens. On the other hand, the spectra of AC showed that AC had a homogenous chemical structure due to its high content of carbon atom comparing the other samples.

As a result of abundant organic and inorganic contents of sewage sludge, FTIR spectra of raw material and adsorbents demonstrated the presence of various functional groups such as aliphatic, carboxylic, aromatic, silicon and phosphorous which are based on various components of bacterial residues, carbohydrates, proteins, lipids and ash.

Figure 3 presents the micrographs of the surface properties of SWS, CSWS, ASWS and AC. The structure of raw sludge (Figure 3a) was dense and there were almost no pores on it. The structure of raw material became significantly different due to the decomposition of organic matters after the carbonization and activation process. Commercial activated carbon has a more porous structure and higher surface area than other sewage sludge based adsorbents.

It can be seen easily from the micrographs that the surface of carbonized product (Figure 3b) was collapsed and some pores appeared. On the other hand, after the chemical activation process, pores in various shapes and sizes (Figure 3c) were formed due to some ZnCl_2 evaporation from carbon skeleton and interaction between ZnCl_2 and other compounds (*e.g.*, H_2O) of sludge during the activation process. Moreover, opening of the closed gaps previously occupied by ZnCl_2 also contributed to porous structure subsequent to the washing process. On the other hand, on the surface of commercial activated carbon

pores were more distributed regularly, and pore volumes and the number of pores were higher than those of activated sewage sludge (Figure 3d).

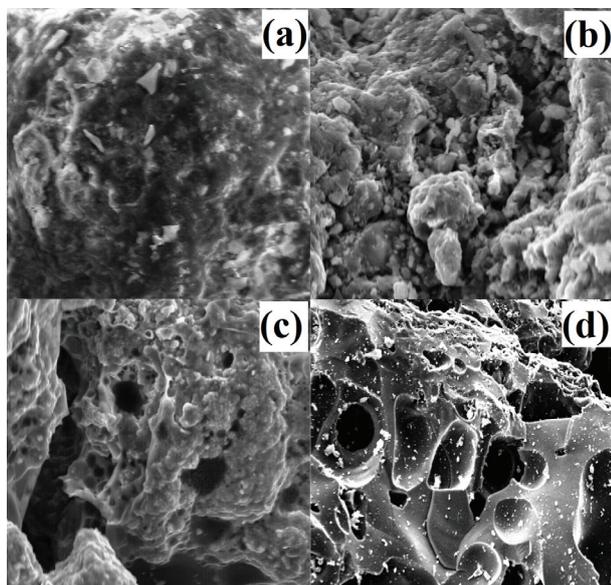


Figure 3. SEM images of SWS (a), CSWS (b), ASWS (c) and AC (d).

The BET analysis strongly supported the SEM micrographs. According to the BET results, the surface area of the materials increased considerably from SWS to ASWS. BET surface area values of SWS, CSWS, ASWS and AC were 0.94, 19.2, 348.93 and 899.95 $\text{m}^2 \text{g}^{-1}$, respectively. It was very clear that chemical activation method was the best option for the production of adsorbents with high surface area. The value of 348.93 $\text{m}^2 \text{g}^{-1}$ was very notable when it compared with other studies in the literature. So far, many investigations on sewage sludge based adsorbents features different BET values in a wide range of 7-1705 $\text{m}^2 \text{g}^{-1}$ [37].

Before the batch adsorption experiments, in order to determine the optimum adsorption time and adsorption kinetics, the effect of contact time on adsorption was evaluated at 25 °C by using 100 mg L^{-1} dye solution. As can be seen in Figure 4, RBBR uptake increased rapidly at the beginning of adsorption process with the increasing contact time and thereafter reached to the equilibrium. The data of the SWS were not included in the graph due to its very low value that restricted the comparison of other adsorbents. The adsorption trends were very similar for AC and ASWS, along with SWS and CSWS, separately. AC showed the best adsorption performance while SWS showed worst performance among the four samples.

The minimum contact time required to reach to the equilibrium was found as 60 min for both of sewage sludge based adsorbents similarly to commercial activated carbon. Thus, the contact time was fixed at this value to make sure that equilibrium was established for the other batch adsorption experiments. Figure 4 indicated that the extent of adsorption increased up to a particular value with increasing time, after which no further increase occurred for the adsorption of RBBR. Furthermore, when adsorbents were saturated by RBBR after about 70 min, a desorption process started.

Kinetic parameters calculated from Figure 4 for the adsorption of RBBR onto adsorbents are listed in Table 3. The results showed that the adsorption process better fitted to the pseudo-second order kinetic model than the pseudo-first order kinetic model for all adsorbents samples. The values of Q_e agreed well with the experimental data (Q_{exp}) for the pseudo-second order kinetic model. The correlation coefficients of pseudo-second-order kinetic model were also higher than that of the pseudo-first order kinetic

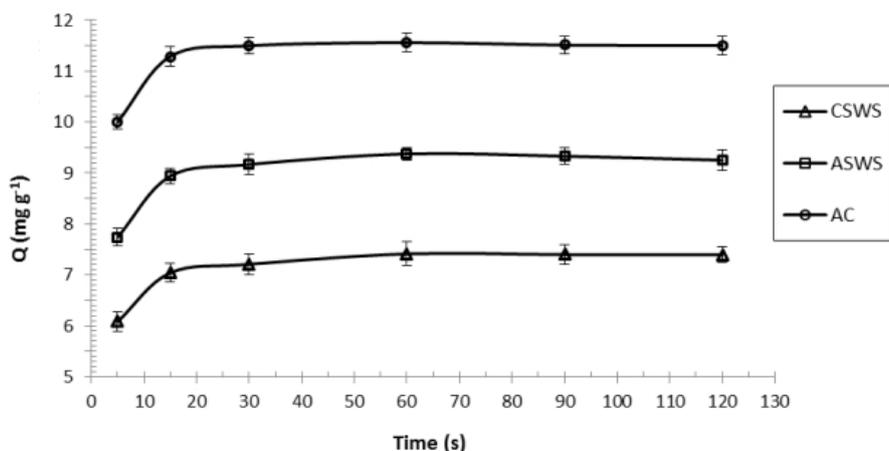


Figure 4. Adsorption capacities of RBBR onto the adsorbents.

Table 3. Pseudo-first-order, Pseudo-second-order kinetic models, Freundlich and Langmuir isotherms constants and correlation coefficients

Adsorbent	$Q_{e(\text{exp})} / \text{mg g}^{-1}$	Pseudo-first-order			Pseudo-second-order		
		$Q_{\text{cal}} / \text{mg g}^{-1}$	k_1 / min^{-1}	R^2	$Q_{\text{cal}} / \text{mg g}^{-1}$	$k_2 / \text{g (mg min)}^{-1}$	R^2
SWS	0.557	0.124	0.006	0.127	0.590	0.287	0.984
AC	11.561	0.294	0.017	0.609	11.534	0.515	0.999
CSWS	7.413	0.601	0.035	0.947	7.451	0.199	0.999
ASWS	9.376	1.390	0.017	0.675	9.319	0.343	0.999

Adsorbent	Freundlich constants			Langmuir constants		
	$K_f / \text{mg g}^{-1}$	n	R^2	$Q_{\text{max}} / \text{mg g}^{-1}$	$b \times 10^3 / \text{L g}^{-1}$	R^2
SWS	0.019	1.51	0.870	0.87	6.76	0.964
AC	1.469	0.998	0.866	109.89	13.82	0.923
CSWS	0.138	0.947	0.973	34.60	4.27	0.978
ASWS	0.296	0.962	0.974	72.99	4.20	0.984

model. As can be seen from Table 3, Q_e values from the pseudo-first order kinetic model were not in agreement with experimental data although the correlation coefficient of CSWS was quite close the value of 1, therefore the adsorption process did not comply with this model. According to these results, adsorption of RBBR onto adsorbents was based on chemisorption mechanisms with a rate-limiting exchange reaction step, which controlled by adsorption process due to inter-particle diffusion [63,64].

Figure 5 shows the amount of adsorbed RBBR onto the adsorbents at equilibrium. Experimental data was plotted as a function of the equilibrium concentration of the standard dye solutions. The data of the SWS were not included in the graph due to its very low value that restricted the comparison of other adsorbents. Adsorption capacity of ASWS increased quite linearly with increasing initial concentration of

RBRR at the equilibrium time similarly to AC. However, unlike ASWS, the adsorbed amount of dye for CSWS increased with lower slope after initial dye concentration of 60 mg L^{-1} . The reason of this situation was due to limited pore structure devoid of mesopore and micropore formations and with a low surface area of CSWS.

According to the batch experimental results, both of the sewage sludge based adsorbents had a maximum dye adsorption capacity of 4.95 (SWS), 54.4 (CSWS), 71.14 (ASWS) and 92.3% (AC) at 20 mg L^{-1} dye concentration. These values were slightly higher than other initial dye concentrations because of rapidly increasing pore saturation with the increasing concentrations at the same conditions. On the contrary, adsorbed percentage of dye generally increased with the increasing concentrations of RBRR and, the adsorption capacities of SWS, CSWS,

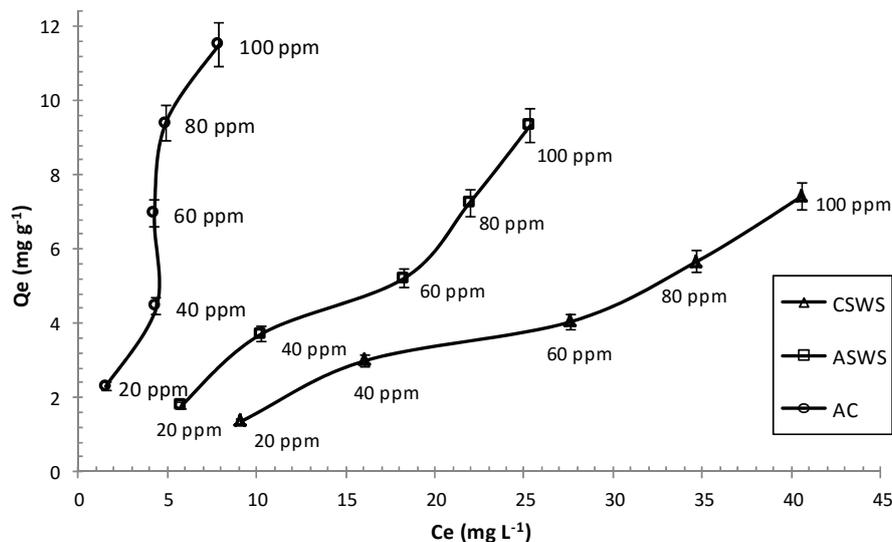


Figure 5. Adsorbed amount of the dye stuff by per unit weight of the adsorbents at different equilibrium of standard solution concentrations.

ASWS and AC were found as 3.46, 59.42, 74.65 and 92.11% at initial dye concentration of 100 mg L^{-1} , respectively.

Adsorption isotherms are very important for the design of adsorption systems since they represent how the dye molecules are partitioned between the adsorbent and liquid phase at equilibrium as a function of concentrations. In this study, obtained equilibrium data for the adsorption of RBBR onto adsorbents were analyzed by considering the Freundlich [61] and Langmuir [62] model equations and isotherms. It was observed from the isotherm charts that both models indicated a decent representation of the experimental results by linear Langmuir or Freundlich isotherm equations. However, according to the regression coefficients (R^2), Langmuir isotherm provided better conformity to the equilibrium data than that of Freundlich isotherm. Freundlich and Langmuir isotherm constants were also listed in Table 3 for the batch adsorption experiments along with kinetic parameters.

As can be seen from Table 3, K_f and Q_{max} values of ASWS indicated that the adsorption capacity were found higher than that of CSWS. Moreover, these values were significantly close to the experimental values. Furthermore, n and b values denoted that ASWS had higher sorption intensity and affinity energy than CSWS. Based on the n values ranging between 1 and 10 (very close to the value of 1, with the exception of SWS), it can be concluded that the adsorption process was very favorable. The results indicated that AC showed great consistency with both Freundlich and Langmuir isotherms with a correlation coefficient of 0.866 and 0.923, respectively. Moreover, it had the highest Q_{max} value of 109.89 mg g^{-1} for Langmuir among the four samples. The isotherm plots also showed that the Langmuir isotherm provided the best fit with a correlation coefficient of 0.978 for CSWS. On the other hand, the correlation value of

the Freundlich isotherm (0.973) was quite close to this value. Therefore, the adsorption characteristics of CSWS could be explained with both Langmuir and Freundlich isotherms, as homogeneous surface and monomolecular or heterogeneous surface adsorption mechanisms, respectively.

On the other hand, it was very clear from Table 3 that the adsorption characteristics of ASWS were in accordance with both Freundlich and Langmuir isotherms due to very close regression coefficients. Therefore, it could be inferred that the adsorption characteristics of ASWS was a heterogeneous surface system with the interaction between adsorbed molecules and exponential distribution of active centers in the adsorbent. Negatively charged reactive RBBR compounds were affected with an electrostatic attraction towards positively charged adsorbent surface and thereby above-mentioned adsorption phenomena occurred.

However, if a system is explained with the Langmuir isotherm, it is very important to determine the dimensionless separation factor [65] called the equilibrium parameter (R_L), represented by Eq. (6):

$$R_L = \frac{1}{1 + bc_0} \quad (6)$$

where b (mg L^{-1}) is the Langmuir constant and c_0 (mg L^{-1}) is the initial dye concentration. The value of R_L shows the kind of the Langmuir isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Figure 6 presents the R_L values of the adsorption process at different initial dye concentrations for all adsorbents. As can be seen in Figure 6, all R_L values were between 0 and 1 and decreased with increasing dye concentration from one to zero. These values demonstrated that the adsorption behavior of RBBR dye onto all adsorbents

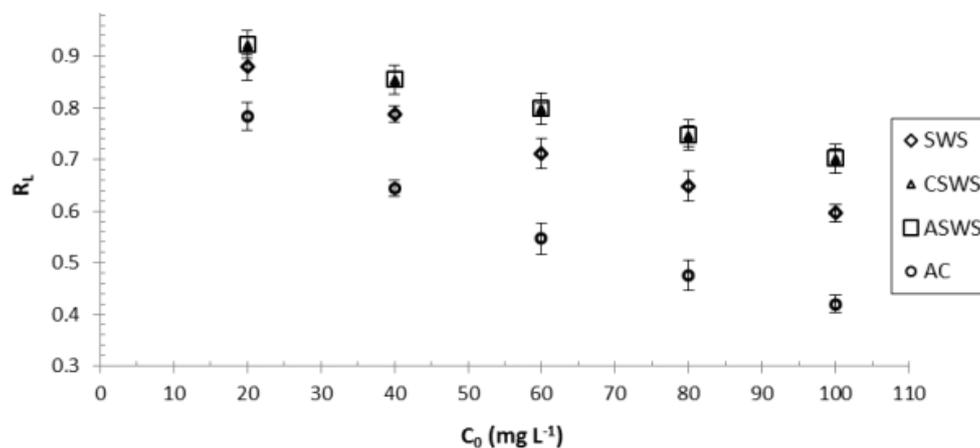


Figure 6. Dimensionless separation factor of RBBR dye adsorption onto adsorbents.

was significantly favorable and increasingly irreversible with increasing concentration of adsorbate.

Table 4 presents a summary of related studies about RBBR adsorption onto different adsorbents and their adsorption performance comparing the results of this study. Considering the previous studies in Table 4 about the RBBR uptake by activated carbons and adsorbents obtained from alternative sources, CSWS and ASWS showed considerable performance.

close performance to commercial activated carbon in terms of adsorption efficiency. As a result, the present study proved that sewage sludge, a problematic by-product of wastewater treatment plant, could be effectively used in treatment of the same wastewater streams after it was activated thermally and chemically *via* pyrolysis in an eco-friendly recycle.

Table 4. Comparison of adsorption capacity of various adsorbents for the adsorption of RBBR

Adsorbent	Adsorption capacity, mg g ⁻¹ or %	pH	Ref.
ZnO fine powder	345 mg g ⁻¹	4	[4]
Sawdust based activated carbon	368.5 mg g ⁻¹	10.7	[16]
Jatropha curcas pods based activated carbon	95%; 50 mg L ⁻¹ -25 mL dye:0.2 g AC	3	[37]
Immobilized <i>Scenedesmus quadricauda</i>	48.3 mg g ⁻¹	2	[44]
Rambutan peel based activated carbon	78.38%; 100 mg L ⁻¹ -200 mL:0.3 g AC	-	[45]
Peanut hull based activated carbon	149.25 mg g ⁻¹	-	[46]
MgO nanoparticles	166.7 mg g ⁻¹	8	[47]
Polyaniline/bacterial extracellular polysaccharides composite	361.82 mg g ⁻¹	3	[48]
Mangosteen peel based activated carbon	80.35%; 100 mg L ⁻¹ -200 mL dye:0.3 g AC	Natural value	[49]
Pine cone based activated carbon	>98%; Different initial dye concentration:0.1 g AC	2 and 11	[50]
Polyurethane-type foam prepared from peanut shell	5 mg g ⁻¹	3	[51]
Red mud	27.8 mg g ⁻¹	2	[52]
Metal hydroxide sludge	91 mg g ⁻¹	7	[53]
Carbonized sewage sludge	34.60 mg g ⁻¹	3	This study
Activated sewage sludge	72.99 mg g ⁻¹	3	This study

CONCLUSIONS

This study demonstrated that chemically activated adsorbents (ASWS) could be employed as effective adsorbents for the removal of reactive RBBR dye from wastewater streams. SEM micrographs of the adsorbents proved that chemical activation is an effective way to manufacture useful high porosity adsorbents. Chemical analysis of adsorbents showed that there were many functional groups that are very important for the nature of adsorption process on the surface of adsorbents, and these compounds vary due to used raw material. The adsorption capacity calculated from kinetic models was quite closer to the experimental data, which indicated that the pseudo first-order was a suitable model to explain the RBBR adsorption kinetics. On the other hand, R^2 values from the plots of Langmuir and Freundlich models indicated that the Freundlich isotherm was a more suitable model to describe the RBBR dye adsorption. In all cases, ASWS showed better performance than that of CSWS due to its highly porous structure and high surface area. Moreover, ASWS exhibited quite

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NAUČNI RAD

UKLANJANJE REAKTIVNE BOJE REMAZOL BRILLIANT BLUE R IZ VODENIH RASTVORA ADSORBENTOM NA BAZI OTPADNOG MULJA IZ ANAEROBNE DIGESTIJE

U ovom radu analiziran je adsorbent dobijen iz otpadnog mulja hemijskom i termalnom aktivacijom. Eksperimenti su izvedeni u cevastoj peći pri brzini zagrevanja od na 20 °C min⁻¹ na temperaturi od 550 °C i sa protokom azota od 400 mL min⁻¹ za 1 h. Šaržni eksperimenti su izvedeni sa rastvorima boje Remazol Brilliant Blue R različitih koncentracija korišćenjem adsorbenta dobijenog iz otpadnog mulja i komercijalnog aktivnog uglja. Maksimalni kapaciteti adsorpcije iz rastvora u kojima je koncentracija boje bila 100 mg L⁻¹ na karbonizovanom otpadnom mulju (CSWS), aktiviranom otpadnom mulju (ASWS) i komercijalnom aktivnom uglju su bile: 7,413; 9,376 i 11,561 mg g⁻¹, redom. Za objašnjavaње mehanizma adsorpcije korišćene su Frojndlihova i Lengmirova adsorpciona izoterma i kinetički modeli pseudo prvog i drugog reda. Langmuirova adsorpciona izoterma koja ima adsorpcione kapacitete od 34,60 mg g⁻¹ za CSWS i 72,99 mg g⁻¹ za ASWS, bolje fituje eksperimentalne podatke od Frojndlihove izoterme. Model pseudo-drugog reda koji je imao adsorpcione kapacitete od 7,451 mg g⁻¹ za CSWS i 9,319 mg g⁻¹ za ASWS, pokazao se jako dobrim u objašnjenju kinetike adsorpcije, sa jako visokim vrednostima regresionih koeficijenata.

Ključne reči: otpadni mulj, karbonizacija, aktivni ugalj, adsorpcija, Remazol Brilliant Blue R.