

# STUDY ON THE RECYCLE OF STEEL SLAG AS AN ADSORBENT FOR COD REMOVAL IN PULP MILL WASTEWATER

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Abstract. This study aims to characterize and investigate steel slag for the removal of its persistent organic pollutants (measured as COD) from pulp mill wastewater. Steel slag and its NaOH-modified states were characterized by Fourier-transform infrared spectroscopy (FT-IR), Brunauer-Emmett-Teller (BET) surface area analysis, Barrett-Joyner-Halenda (BJH) pore size, and volume analysis. Batch adsorption experiments were conducted to investigate the COD adsorption of slag-based adsorbents. The modification of NaOH was found to improve the COD adsorption capacity (by 1.5 times) of steel slag by generating hydroxyl and carboxyl groups and enlarging the specific surface area and pore size in the steel slag particles. In batch experiments, the suitable conditions for COD adsorption on NS (steel slag) and MS20 (2 M NaOH-modified steel slag) were determined to be pH 6 - 8, contact time 90 minutes, and adsorbent dosage 20 g/L. Langmuir and Freundlich adsorption isotherm models satisfactorily described the adsorption of COD on both NS and MS20 with a good correlation. According to the Langmuir isotherm, the maximum COD adsorption capacity of NS and MS20 were 5.16 and 6.87 mg/g, respectively. Column experiments demonstrated that NS and MS20 had promising potential for COD treatment in pulp mill effluent. According to the column results, 20 g of NS or MS20 was able to keep 300 mL or 525 mL of 125 mg/L COD wastewater, respectively, reaching the threshold of the National Technical Regulation on Industrial Wastewater QCVN 40:2021/BTNMT.

*Keywords:* steel slag, persistent organic pollutants, pulp mill wastewater, adsorption, adsorption column, NaOH modification.

Classification numbers: 3.3.2, 3.4.2.

## **1. INTRODUCTION**

Recently, steel manufacturing is one of the most important and fast-growing industries due to the increasing demand for its overall development. Steel-making slag (or steel slag), which is a by-product from the steel-making process, is massively generated at a proportion of 10 - 15 %

by weight of the produced slag [1]. By the Fact sheet of the World Steel Association in April 2021, the generation of steel slag is reported at 400 kg/l ton of steel [2]. Landfill disposal is the most commonly used method for steel slag disposal but it comes with large areas of land use and expensive cost for transportation. Besides, the improper and unplanned landfilling may pose another risk of leaching heavy metals into farmland and rivers [3]. Hence, other novel approaches that have been tried to deal with this by-product are following the reuse or recycle pathways. In the field of civil engineering, steel slag has been reused as an aggregate supplement for concrete and cement production for road construction, backfill, earth cover, and embankment [4-6]. Regarding wastewater remediation, steel slag has been investigated for its adsorption capacity towards dyes, phosphate, nitrate, and ammonia [7 - 11]. Cheng et al. concluded in their study that salicylic acid-methanol modified steel slag achieved an adsorption capacity of 41.62 mg/g for methylene blue via chemical adsorption [8]. Alkaline characteristic and high  $Ca^{2+}$ content were key factors for P removal up to 99 % under optimum conditions, as concluded in a study by Vu et al. [10]. Not to mention that using secondary materials or by-products from industry like steel slag as adsorbents offers many benefits by reducing costs and reusing waste materials for a beneficial application.

On the other hand, effluent from pulp and paper production is well known not only for generating large volumes but also for carrying extremely high toxic loads [12, 13]. This wastewater is characterized by intense color, high chemical oxygen demand (COD) and biological oxygen demand (BOD), low biodegradability, with various types of organic and inorganic compounds [14]. These compounds may include non-biodegradable organic materials, chlorinated compounds, metals, resin acids, chlorinated hydrocarbon, and persistent organic pollutants (POPs) such as phenols, sterols, dioxins, and furans [15]. Due to their persistent and non-biodegradable characteristics, these compounds consistently account for 40 % of the total organic matter content of the effluent from pulp mill industries [16]. These pollutants are highly lethal to aquatic systems, polluting the food chain through contaminated fishes, and causing severe effects and skin disorders in case of exposure [17]. A variety of techniques for the removal of highly toxic organic compounds have drawn significant attention. The methods that have been employed are coagulation, filtration with coagulation, precipitation, ozonation, adsorption, ion exchange, reserve osmosis, and advanced oxidation processes [18]. Among those techniques, the adsorption process using solid adsorbent is one of the most efficient approaches for the treatment and removal of organic content in wastewater due to its simple design, low investment cost and low land requirement. A number of studies have been conducted to investigate COD removal via adsorption which mostly focused on using activated carbon as an adsorbent [19 - 22]. However, there is still limited information on the COD adsorption ability of secondary materials such as steel slag towards organic contamination.

From the foregoing, this study aims: first to measure the kinetics and equilibrium adsorption of COD by steel slag at its natural stage (NS) and NaOH-modified steel slag (MS) in batch and column experiments using real effluent from pulp mill industry, and second, to determine the volume of water can be treated with the NS and MS in column experiments. The novelty of this study is the overall information on the COD adsorption behavior of steel slag and the effect of NaOH modification on its adsorption capacity.

## 2. MATERIALS AND METHODS

## 2.1. Materials

Steel slag was collected from Formosa Ha Tinh Steel Corporation. The steel slag sample is composed of CaO (30 - 45 %), SiO<sub>2</sub> (24 - 45 %), and Al<sub>2</sub>O<sub>3</sub> (8 - 22 %). The sample has a specific weight of 2.45 to 2.55 g/cm<sup>3</sup> with various particle sizes from 0.1 to 20 mm. The steel slag was crushed and sieved to a narrow particle size from 0.25 to 0.5 mm. The sieved material was then washed and dried in an oven at 105 °C for 2 hours to completely remove the humidity (NS). NaOH modified NS was prepared by mixing 50 g of the material with 100 mL of NaOH at various concentrations of 0.5 M (MS05), 1 M (MS10), 2 M (MS20), 3 M (MS30), 4 M (MS40), and 5 M (MS50).

Pulp mill wastewater was collected into the primary settling tank (after screening and before biological treatment) of the WWTP of An Hoa Pulp Mill Factory. Wastewater from An Hoa Pulp Mill is reddish brown in color and has a COD concentration of  $1680 \pm 200 \text{ mg/L}$ .

## 2.2. Characterization

Fourier transform infrared (FTIR) spectra of steel slag (NS) and modified (MS) samples were recorded with an Agilent Cary FTIR 630 instrument (United State) using the KBr disc method to demonstrate sample characterization. The scan range was set from 400 to 4000 cm<sup>-1</sup>.

The samples were degassed at 200  $^{\circ}$ C for 12 hours under vacuum before the surface area and porosity measurements. The Brunauer-Emmet-Teller (BET) method was used to determine the surface area by N<sub>2</sub> adsorption isotherm at 77.3 K using a Tristar II Plus (Micromeritics, United States). The Barrett-Joyner-Halenda (BJH) method was employed to calculate the total pore volume and average pore width.

#### 2.3. Batch adsorption experiments

Batch experiments were conducted by immersing a certain amount of adsorbent in contact with 50 mL of wastewater inside a 100 mL conical flask rotating at 150 rpm and 30 °C inside an incubated shaker (Lab Companion, United States). The test solution was diluted from the pulp mill wastewater into various stages of COD concentration upon the design of each batch experiment.

The effect of NaOH modification on COD adsorption was tested under the following experimental conditions: pH 6, contact time 2 hours, each adsorbent 2 g in a wastewater solution containing 160 mg/L COD. A contact time of 2 hours was chosen to ensure COD adsorption equilibrium was reached according to a previous study [21]. Due to its heavy specific weight compared to other adsorbents, 2 g of steel slag adsorbent was selected in batch tests with 50 mL of solution. The solution at pH 6 and 160 mg/L of COD was used for characterization of the effluent from the pulp mill.

The effect of adsorbent dosage was investigated by performing batch experiments at pH 6 for a contact time of 2 hours with various adsorbent dosages of 0.05, 0.1, 0.25, 0.5, 1, 1.5, and 2 g (corresponding to 1, 2, 5, 10, 20, 30, and 40 g/L). The influence of pH was also investigated under similar conditions but the pH was set at different stages of 2, 4, 6, 8, and 10, adjusted dropwise with HCl and NaOH. The adsorption kinetics was investigated with an adsorbent dosage of 2 g at pH 6 and a COD concentration of 125 mg/L at different time intervals (for 15, 20, 30, 60, 90, 120, 180, and 240 minutes). The effect of initial COD concentrations from 100 to 1800 mg/L was also examined using various batches at different COD concentrations. The suspension after each batch was filtered and the filtrate was analyzed for COD according to

TCVN 6491:1999 by Dichromate Method [23]. During batch experiments, the pH value was measured by a pH meter (HI 2211, Hanna Instrument, United State). The amount of COD adsorbed at equilibrium,  $q_e (mg/g)$ , was calculated as the equation below:

$$q_e = \frac{(\mathcal{C}_o - \mathcal{C}_e).V}{m} \tag{1}$$

where  $C_o$  is the initial concentration of COD (mg/L),  $C_e$  is the equilibrium concentration of COD (mg/L), V is the volume of solution (L), and m is the adsorbent mass (g). The removal efficiency ( $\eta$ ) was calculated using the following equation:

$$\eta (\%) = \frac{(c_o - c_e)}{c_o} \times 100$$

The COD adsorption onto steel slag adsorbents was modeled by fitting the experimental data with Langmuir (eq. 3) and Freundlich (eq.4) adsorption isotherms.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where  $q_m$  is the maximum COD adsorption capacity (mg/g) and  $K_L$  is the Langmuir constant (L/mg) relating to the energy of adsorption.

$$q_e = K_F \times C_e^{1/n} \tag{4}$$

where  $K_F$  is the Freundlich constant  $(mg/g)(L/mg)^{1/n}$  and n is the dimensionless Freundlich constant.

For the kinetics of adsorption, the amount of COD adsorbed at time t  $(q_t, mg/g)$  was calculated as follows:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{5}$$

where  $C_t$  is the concentration of COD at time t (mg/L). The kinetic adsorption of COD on steel slag adsorbents was modeled by fitting the experimental data with pseudo-first order (eq. 6) and pseudo-second order (eq. 7) equations:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

where  $k_1$  is the rate constant for the pseudo-first order equation (1/h).

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{7}$$

where  $k_2$  is the rate constant for the pseudo-second order equation (g/mg.h).

#### 2.4. Column experiments

A 25 mL glass tube (2 cm in diameter and 10 cm in height) packed with 20 g of steel slag adsorbents was used to simulate a filter column for this experiment. Pulp mill wastewater with 125 mg/L of COD, which is representative of the final effluent from the WWTP, was passed through the column at a flow rate of 2.5 mL/min in the up-flow direction controlled by an Iwaki Metering Pump (Model EHN-C36VH4R, Iwaki Co., Ltd, Tokyo, Japan). At the bottom of the column, a thin layer of cotton filer was placed to prevent the material from falling into the pipe. Before the wastewater was fed to the column, the column was prefilled with distilled water

during the packing of material to prevent trapped bubbles. The samples were collected after 10 minutes since the feeding started.

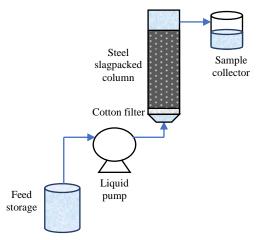


Figure 1. Column experiment diagram.

## **3. RESULTS AND DISCUSSION**

#### 3.1. Comparison of characteristic and adsorption capacity between steel slag materials

The FTIR spectra of steel slag (NS) and its NaOH-modified materials are presented in Figure 2. According to the FT-IR patterns in Figure 2, samples from NS to MS30 shared similar bands which significantly appeared at 3400 cm<sup>-1</sup>, 1450 cm<sup>-1</sup>, and 1000 cm<sup>-1</sup>. The broadband at 3400 cm<sup>-1</sup> was attributed to the hydroxyl stretching mode, while the 1000 cm<sup>-1</sup> might be assigned to hydroxyl deformation modes and also the characteristic of Si-O stretching of silica and silicates [24]. These two patterns confirmed the presence of hydroxides and oxyhydroxides in the slag samples. The very strong peak appearing at 1450 cm<sup>-1</sup> corresponded to the C-O stretching of  $CO_3^{2^2}$  ion [25]. The effect of NaOH modification on steel slag can be observed at the enhancement of intensity in hydroxyl stretching band (3400 cm<sup>-1</sup>, and 1000 cm<sup>-1</sup>) and C-O stretching (1450 cm<sup>-1</sup>) compared to the NS sample. This was the result of more metal hydroxides being produced when the steel slag was blended with the NaOH solution. The sharp bands recorded at 875 cm<sup>-1</sup>, which represented the deformation modes of C-O vibrations, were also detected for the NaOH-modified samples only [25].

The porosity of slag-based adsorbents was illustrated in Table 1. The porosity of steel slag began to improve at 1 M NaOH concentration. The S<sub>Bet</sub> of MS10, MS20, and MS30 was 2.1193 m<sup>2</sup>/g, 2.4150 m<sup>2</sup>/g, and 2.4693 m<sup>2</sup>/g, respectively. The specific surface area of MS20 and MS30 was around 1.3 times that of the NS. The pore volume was also enlarged after the steel slag was modified with 2 M and 3 M NaOH (0.007 to 0.01 cm<sup>3</sup>/g). The excessive concentration of NaOH, however, was not proportional to the enhancement of the porosity of the steel slag. According to the results, there was a slight decrease in S<sub>Bet</sub> and V<sub>P</sub> when the C<sub>NaOH</sub> reached 4M (S<sub>Bet</sub> = 2.2206 m<sup>2</sup>/g, V<sub>P</sub> = 0.009 cm<sup>3</sup>/g) and 5 M (S<sub>Bet</sub> = 2.23076 m<sup>2</sup>/g, V<sub>P</sub> = 0.01 cm<sup>3</sup>/g). The improvement of the porosity might be the result of chemical activation to develop micropores in the adsorbent particle [26]. The surface area enlargement by NaOH modification was also reported in a study by Xiu *et al.* in which the S<sub>Bet</sub> of persimmon power-formaldehyde resin increased 2 times (0.23 m<sup>2</sup>/g to 0.47 m<sup>2</sup>/g) [27].

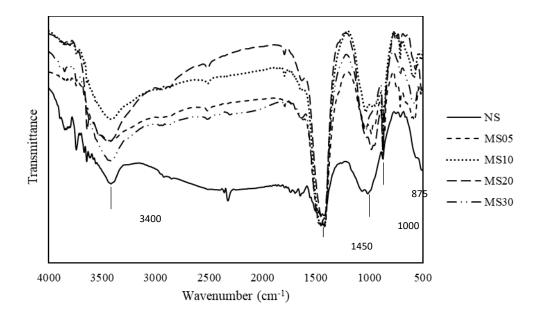


Figure 2. FT-IR spectra of steel slag (NS) and its NaOH modified materials.

Table 1. BET surface area ( $S_{BET}$ ) and pore volume ( $V_P$ ) of steel slag (NS) and NaOH modified steel slag (MS).

Sample	$S_{BET} (m^2/g)$	$V_P(cm^3/g)$	Average pore width (nm)
NS	1.8997	0.007638	16.5496
MS05	1.8827	0.008074	16.6998
MS10	2.1193	0.009054	16.7674
MS20	2.4150	0.010193	16.9833
MS30	2.4693	0.010254	17.1674
MS40	2.2206	0.009248	16.7853
MS50	2.2376	0.010338	17.6076

The effect of NaOH concentration for steel slag modification on COD adsorption capacity is presented in Figure 3. The *q* value measured at  $C_{NaOH}$  of 0 was the adsorption capacity of steel slag at its natural state. According to the results, the NaOH concentration for modification has both positive and negative impacts on the COD adsorption of steel slag. The adsorption capacity was improved noticeably when the NaOH concentration increased from 0 to 2 M. The *q* value of steel slag modified with 2 M NaOH (MS20) was 2.36 mg/g, which was around 1.5 times the value of NS. This was possibly the result of the improvement in the surface structure and porosity of MS20 compared to NS, and the formation of metal hydroxide and carboxyl groups as well. The improvement, however, slowed down when the gap between *q* values for steel slag modified at 2 M and 3 M was negligible (2.36 and 2.44 mg/g). An excessive dosage of NaOH for modification even led to a significant decrease in adsorption capacity. The *q* value dropped to 1.52 mg/g at  $C_{NaOH}$  of 4 M, which was more than 1.5 decrement, and eventually bottomed at 1.14 mg/g at  $C_{NaOH}$  of 5 M. The limited adsorption capacity at higher NaOH concentrations can be explained by its impact on the pH solution. The enhancement of COD adsorption by NaOH modification was in good agreement with Nouha *et al.* and Hayati *et al.* [28, 29]. In the research of Nouha *et al.*, 4 M NaOH-treated activated carbon achieved 442.69 mg/g of phenol adsorption capacity, which was 4 times the improvement of the non-treated (110.33 mg/g) [28]. Hayati *et al.* discussed that a variety of oxygen functional groups such as hydroxyl and carboxyl of NaOH modified activated carbon enhanced its dye adsorption capacity in a low pH environment [29]. According to Figure 3, the 3M NaOH-modified steel slag has the highest *q* of 2.44 mg/g, however, the improvement was insignificant from the 2 M NaOH-modified (2.37 mg/g) despite the greater NaOH consumption. Considering the best improvement of adsorption capacity and the less consumption of chemicals at modification, MS20 was preferred as the most suitable modified sample for further investigations.

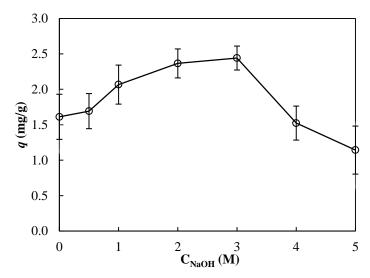
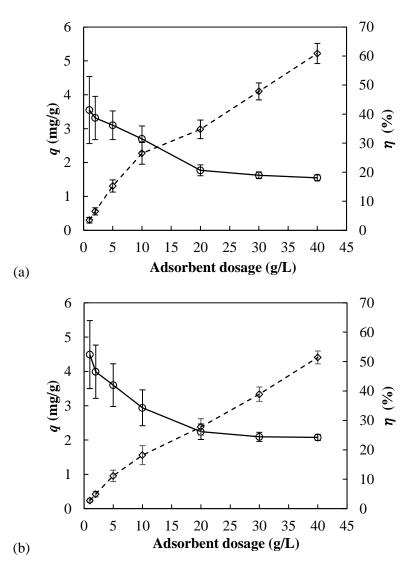


Figure 3. Effect of NaOH activation concentration on COD adsorption capacity of steel slag adsorbents.

#### 3.2. Effect of adsorbent dosage

The effect of adsorbent dosage from 1 to 40 g/L on the COD adsorption on NS and MS20 is presented in Figure 4. According to the results, a similar trend on COD adsorption capacity and removal efficiency was recognized in NS and MS20 materials. Similar to the finding of El-nass *et al.* [19], the change in the amount of material caused an opposite trend between the COD adsorption capacity (q) and removal efficiency ( $\eta$ ). Increasing adsorbent dosage from 1 to 20 g/L led to a slight drop in q value (3.55 to 1.77 mg/g for NS and 4.49 to 2.24 mg/g for MS20). The q value, however, remained stable as the dosage continued to increase from 20 to 40. This trend in q value can be explained by the excessive amounts of adsorbent leading to the unsaturation of adsorbent binding sites. As for the COD removal efficiency, the higher adsorbent dosage resulted in the improvement of COD removal as it presented a substantial contact site from the adsorbents to the target compound despite the unsaturated binding sites. The  $\eta$  value of NS and MS20 increased from 3.49 to 60.68 % and from 2.78 to 51.42 % as the dosage increased from 1 to 40 g/L, respectively.



*Figure 4*. Effect of (a) NS ( $C_o = 101.8 \text{ mg/L}$ ) and (b) MS20 ( $C_o = 161.5 \text{ mg/L}$ ) dosage on COD adsorption capacity (q) and removal efficiency ( $\eta$ ) ( $\circ$ : adsorption capacity,  $\diamond$ : removal efficiency).

#### **3.3. Effect of pH level**

The effect of initial pH on the COD adsorption of NS and MS20 was investigated in the range from 2 to 10 and is presented in Figure 5. The natural pH of the pulp mill wastewater sample was slightly above 6 and was adjusted to a desired value by dropwise addition of HCl and NaOH. For the NS material, from pH 2 to 10, the q value only varied by 0.5 mg/g and reached the peak of 1.51 mg/g at pH 6. However, the ideal pH level for COD adsorption was recorded at pH 8 for MS20 when it achieved 2.38 mg/g, slightly higher than that of pH 6 (2.19 mg/g). This pattern can be explained by the absence of H<sup>+</sup> and OH<sup>-</sup> ions at neutral pH which reduces the occupation of these ions to the binding site of the adsorbent. According to the results, it can be noted that pH range from 6 to 8 could be desirable for COD adsorption on NS

and MS20. Other reports also concluded that the neutral pH condition was favorable for COD adsorption and dye adsorption onto carbon-based materials [19, 30, 31].

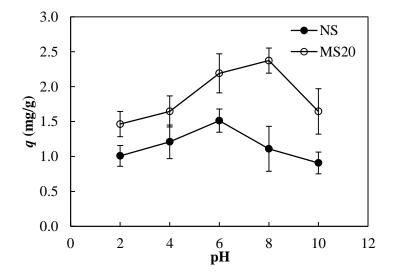


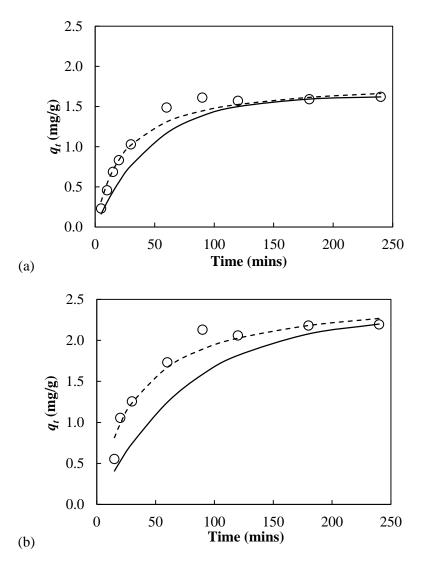
Figure 5. The effect of pH level on the COD adsorption on NS and MS20 materials.

## 3.4. Kinetics of batch COD adsorption

The adsorption kinetics was examined with various stages of contact time from 5 minutes to 240 minutes. The adsorption of COD on both NS and MS20 rapidly increased within the first 90 minutes. The  $q_t$  value reached 1.61 mg/g and 2.13 mg/g for NS and MS20 after 90 minutes of batch adsorption, respectively (Figure 6). The adsorption capacity, however, remained almost stable after 90 minutes to the rest of the longer contact period. As shown in Table 2, the data were in better agreement with the pseudo-second order model ( $R^2 = 0.983$  and 0.992 for NS and MS20, respectively) than with the pseudo-first order model ( $R^2 = 0.820$  and 0.835 for NS and MS20, respectively). This result indicated that chemical adsorption and physical adsorption are both involved in the adsorption of organic contaminants on steel slag materials. This kinetic pattern for COD adsorption on steel slag was similar to the kinetic mechanism for composite and zeolite adsorbent in a study of Halim *et al.* [21].

*Table 2.* Batch kinetic model parameters and coefficient of determination ( $R^2$ ) of the models fitting the data for the adsorption of COD on NS and MS20 at pH 6 (adsorbent dosage of 20 g/L at COD concentration of 125 mg/L).

Adsorbent	Pseudo-first order (PFO)			Pseudo-second order (PSO)			
_	$q_e$	$k_1$	$\mathbf{R}^2$	$q_e$	$k_2$	$\mathbb{R}^2$	
	mg/g	$\min^{-1}$		mg/g	g/mg.min		
NS	0.926	0.021	0.820	1.827	0.023	0.992	
MS20	1.308	0.013	0.835	2.573	0.012	0.983	

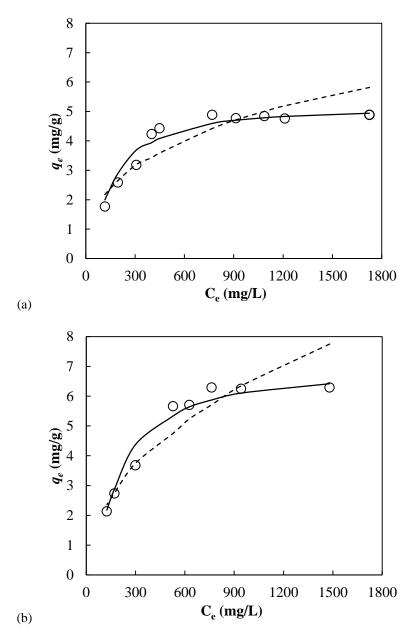


*Figure 6.* Batch kinetic data for COD adsorption on: (a) NS and (b) MS20 (o: experimental data, dashed line: PFO prediction model, solid line: PSO prediction model).

#### **3.5. Batch COD adsorption at equilibrium**

The equilibrium curves for COD adsorption isotherm for NS and MS20 are presented in Figure 7. The data satisfactorily obeyed the Langmuir adsorption model for both NS and MS20 materials with the coefficient of determination ( $\mathbb{R}^2$ ) values of 0.997 and 0.995, respectively (Table 3). The Freundlich adsorption model also describes most of the data from the MS20 with the  $\mathbb{R}^2$  value of 0.921, rather than the data from the NS ( $\mathbb{R}^2 = 0.833$ ). This result indicated that the NaOH modification exhibited the multi-layer adsorbent on the adsorption site of MS20 compared to the monolayer adsorption of NS, leading to higher COD adsorption capacity. The  $q_m$  value for NS and MS20 in COD adsorption were 5.175 and 6.872 mg/g, respectively. In comparison with the results of Halim *et al.* and Omid *et al.*, the COD adsorption capacity of slag-based material was better than zeolite (2.36 mg/g), comparable to the animal horn-based

activated carbon (6.46 mg/g), but still lower than composite material (22.99 mg/g) and commercial activated carbon (37.88 mg/g) [21, 32] (Table 3). According to the Langmuir model,  $R_L$ , the separation factor, describes the favorability of the adsorption process [33]. The  $R_L$  values for COD adsorption on both NS and MS20 were 0.04 to 0.38 and 0.06 to 0.42, respectively, which suggested that the adsorption process is favorable. The Freundlich constant 1/n was under the range between 0.1 and 1 for both materials, which described positive interaction between the organic contaminants and the slag-based adsorbent [33].



*Figure 7.* Batch equilibrium data for COD adsorption on (a) NS and (b) MS20 at pH 6 and the fit of experimental data (0) with Langmuir (solid line) and Freundlich (dashed line) models.

	Langmuir model			Freundlich model			_
Adsorbent	$q_m$ (mg/g)	K <sub>L</sub> (L/g)	$R^2$	$\begin{array}{c} K_{F} \\ (mg/g)(L/mg)^{1/n} \end{array}$	1/n	$\mathbf{R}^2$	Ref.
NS	5.175	0.014	0.997	0.746	0.280	0.833	This
MS20	6.872	0.011	0.995	0.650	0.348	0.921	study
Zeolite	0.818	$1.14 \times 10^{-4}$	0.968	1.27×10 <sup>-5</sup>	1.996	0.805	
Composite adsorbent	22.99	9.4×10 <sup>-4</sup>	0.965	0.064	0.764	0.929	Halim <i>et al</i> . [21]
Activated carbon	37.88	$1 \times 10^{-3}$	0.9819	0.154	0.688	0.9384	[21]
Commercial activated carbon	10.11	0.412	0.999	9.863	-11.820	0.993	Omid
Animal horn- derived activated carbon	6.46	0.248	0.999	13.712	-15.576	0.995	et al. [32]

*Table 3.* Langmuir and Freundlich model parameters and coefficient of determination (R<sup>2</sup>) of the models fitting the data for COD adsorption on NS and MS20, and comparison with other materials.

## 3.5. Column adsorption experiment

The initial COD concentration for wastewater in this column experiment was 125 mg/L, representing the COD in the pulp mill wastewater from the WWTP. The curves from the column experiment for COD adsorption on NS and MS20 are presented in Figure 8. According to the results, the bed volumes of the water treated under the National Technical Regulation on Industrial Wastewater **QCVN 40:2021/BTNMT** for COD by the MS20 (0.525 L) was larger than that by NS (0.3 L) due to its higher COD adsorption capacity (Table 5) [34]. The COD adsorption capacity on the column was lower than that in the batch adsorption because the initial concentration used in the column was much lower than in the the batch experiment.

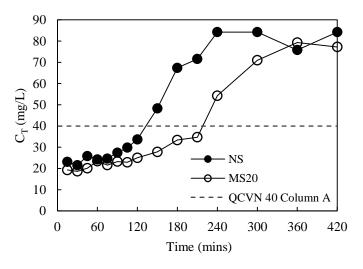


Figure 8. Breakthrough curves for COD adsorption on NS and MS20.

*Table 5.* Bed volume treated by NS and MS20 columns (20 g of adsorbent in a 25mL syringe-based column) to reduce COD concentration to the QCVN40 column A concentration (40 mg/L) and amount of COD adsorbed on NS and MS20.

Filtration flowrate (L/min)	Adsorbent	COD concentration (mg/L)	Bed volume (L)	COD adsorption capacity (mg/g)
0.0025	NS	105	0.300	1.50
0.0025	MS20	125	0.525	3.00

#### 4. CONCLUSIONS

This study has successfully investigated the adsorption potential of steel slag and its modified materials for COD removal from real pulp mill wastewater. The results showed that NaOH modification had a positive effect on the COD adsorption capacity of steel slag. According to the batch results, the suitable conditions for the COD adsorption on slag-based adsorbent included neutral pH (6-8), contact time of 90 minutes, adsorbent dosage of 10 g/L, and initial COD concentration of 400 to 500 mg/L. The COD adsorption on NS was better fitted with the Langmuir isotherm ( $R^2 = 0.997$ ) than the Freundlich isotherm ( $R^2 = 0.833$ ) while MS20 showed good agreement with both models ( $R^2 = 0.995$  and 0.921 for Langmuir and Freundlich, respectively). The maximum COD adsorption capacity for NS and MS20 were 5.175 and 6.872 mg/g, respectively, according to the Langmuir model. A column experiment was performed with 20 g of each material, 125 mg/L COD in the influent, and a flow rate of 2.5 mL/min. According to the column results, 20 g of NS was capable of treating 300 mL of wastewater to the QCVN 40 col A threshold, while MS was able to deal with 525 mL of wastewater with the same results. From this result, COD adsorption is possibly a good pathway to recycle steel slag with promising efficiency.

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#### REFERENCES

- Proctor D., Fehling K., Shay E., Wittenborn J., Green J., Avent C., Bigham R., Connolly M., Lee B. and Shepker T. - Physical and chemical characteristics of blast furnace, basic oxygen furnace, and electric arc furnace steel industry slags, Environmental Science Technology 34 (8) (2000) 1576-1582.
- 2. Steel industry co-products. World Steel Association, 2021
- 3. Song Q., Guo M. Z., Wang L. and Ling T. C. Use of steel slag as sustainable construction materials: A review of accelerated carbonation treatment, Resources, Conservation and Recycling **173** (2021) 105740.

- 4. Jin Wei L., Chew L. H., Choong T., Tezara C. and Yazdi M. Overview of Steel Slag Application and Utilization, MATEC Web of Conferences, Vol. 74, 2016, p. 00026.
- 5. Ahmedzade P. and Sengoz B. Evaluation of steel slag coarse aggregate in hot mix asphalt concrete, Journal of hazardous materials **165** (1-3) (2009) 300-305.
- 6. Panesar D. K.- Supplementary cementing materials, in Developments in the Formulation and Reinforcement of Concrete, Elsevier, 2019, pp. 55-85.
- 7. Xue Y., Hou H. and Zhu S. Adsorption removal of reactive dyes from aqueous solution by modified basic oxygen furnace slag: isotherm and kinetic study, Chemical Engineering Journal **147** (2-3) (2009) 272-279.
- 8. Cheng M., Zeng G., Huang D., Lai C., Liu Y., Zhang C., Wang R., Qin L., Xue W., Song B., Ye S. and Yi H. High adsorption of methylene blue by salicylic acid-methanol modified steel converter slag and evaluation of its mechanism, Journal of Colloid and Interface Science **515** (2018) 232-239.
- 9. Blanco I., Molle P., de Miera L. E. S. and Ansola G. Basic oxygen furnace steel slag aggregates for phosphorus treatment, Evaluation of its potential use as a substrate in constructed wetlands, Water research **89** (2016) 355-365.
- Vu M. T., Nguyen L. N., Hasan Johir M. A., Ngo H. H., Skidmore C., Fontana A., Galway B., Bustamante H., and Nghiem L. D. - Phosphorus removal from aqueous solution by steel making slag – Mechanisms and performance optimisation, Journal of Cleaner Production 284 (2021) 124753.
- 11. Wang S., Yao S., Du K., Yuan R., Chen H., Wang F. and Zhou B. The mechanisms of conventional pollutants adsorption by modified granular steel slag, Environmental Engineering Research **26** (1) (2021) 190352-190350.
- 12. Ashrafi O., Yerushalmi L., and Haghighat F. Wastewater treatment in the pulp-and-paper industry: A review of treatment processes and the associated greenhouse gas emission, Journal of Environmental Management **158** (2015) 146-157.
- 13. Singh A. K. and Chandra R. Pollutants released from the pulp paper industry: Aquatic toxicity and their health hazards, Aquatic Toxicology **211** (2019) 202-216.
- 14. Mazhar S., Ditta A., Bulgariu L., Ahmad I., Ahmed M. and Nadiri A. A. Sequential treatment of paper and pulp industrial wastewater: Prediction of water quality parameters by Mamdani Fuzzy Logic model and phytotoxicity assessment, Chemosphere **227** (2019) 256-268.
- Carvalho Neves L., Beber de Souza J., de Souza Vidal C. M., Herbert L. T., de Souza K. V., Geronazzo Martins K. and Young B. J. Phytotoxicity indexes and removal of color, COD, phenols and ISA from pulp and paper mill wastewater post-treated by UV/H2O2 and photo-Fenton, Ecotoxicology and Environmental Safety 202 (2020) 110939.
- 16. Tsang Y. F., Hua F. L., Chua H., Sin S. N. and Wang Y. J. Optimization of biological treatment of paper mill effluent in a sequencing batch reactor, Biochemical Engineering Journal **34** (3) (2007) 193-199.
- 17. Kumar A. and Chandra R. Biodegradation and toxicity reduction of pulp paper mill wastewater by isolated laccase producing Bacillus cereus AKRC03, Cleaner Engineering and Technology **4** (2021) 100193.
- 18. Nageeb M. Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater, 2013.

- 19. El-Naas M. H., Al-Zuhair S. and Alhaija M. A. Reduction of COD in refinery wastewater through adsorption on date-pit activated carbon, Journal of Hazardous Materials **173** (1) (2010) 750-757.
- Mohammad-pajooh E., Turcios A. E., Cuff G., Weichgrebe D., Rosenwinkel K. H., Vedenyapina M. D., and Sharifullina L. R. - Removal of inert COD and trace metals from stabilized landfill leachate by granular activated carbon (GAC) adsorption, Journal of Environmental Management 228 (2018) 189-196.
- 21. Halim A. A., Aziz H. A., Johari M. A. M., and Ariffin K. S. Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment, Desalination **262** (1) (2010) 31-35.
- 22. GilPavas E. and Correa-Sanchez S. Assessment of the optimized treatment of indigopolluted industrial textile wastewater by a sequential electrocoagulation-activated carbon adsorption process, Journal of Water Process Engineering **36** (2020) 101306.
- 23. Ministry of Science Technology and Environment TCVN 6491:1999 Water Quality Determination of the chemical oxygen demand, 1999.
- 24. Navarro C., Díaz M. and Villa-García M. A. Physico-Chemical Characterization of Steel Slag. Study of its Behavior under Simulated Environmental Conditions, Environmental Science & Technology **44** (14) (2010) 5383-5388.
- 25. Miller F. A. Amides, Carboxylate Ion, and C-O Single Bonds, in: Mayo D. W., Miller F. A. and Hannah R. W., Course Notes on the Interpretation of Infrared and Raman Spectra, John Wiley & Sons Inc., New Jersey, 2004 pp. 205-215.
- 26. Kim D. W., Kil H. S., Nakabayashi K., Yoon S. H., and Miyawaki J. Structural elucidation of physical and chemical activation mechanisms based on the microdomain structure model, Carbon **114** (2017) 98-105.
- 27. Xie F., Fan R., Yi Q., Zhang Q. and Luo Z. NaOH Modification of Persimmon Powderformaldehyde Resin to Enhance Cu2+ and Pb2+ Removal from Aqueous Solution, Procedia Environmental Sciences **31** (2016) 817-826.
- 28. Nouha S., Souad N. S., and Abdelmottalab O. Enhanced adsorption of phenol using alkaline modified activated carbon prepared from olive stones, Journal of the Chilean Chemical Society **64** (2019) 4352-4359.
- 29. Hayati B. and Mahmoodi N. M. Modification of activated carbon by the alkaline treatment to remove the dyes from wastewater: Mechanism, isotherm and kinetic, Desalination and water treatment **47** (2012) 322-333.
- 30. Parande A. K., Sivashanmugam A., Beulah H. and Palaniswamy N. Performance evaluation of low cost adsorbents in reduction of COD in sugar industrial effluent, Journal of Hazardous Materials **168** (2-3) (2009) 800-805.
- 31. Mittal A., Gajbe V. and Mittal J. Removal and recovery of hazardous triphenylmethane dye, Methyl Violet through adsorption over granulated waste materials, Journal of Hazardous Materials **150** (2) (2008) 364-375.
- 32. Aluyor E. O. and Badmus O. A. M. COD removal from industrial wastewater using activated carbon prepared from animal horns, African Journal of Biotechnology 7 (21) (2008) 3887-3891.

- 33. Rusmin R., Sarkar B., Liu Y., McClure S. and Naidu R. Structural evolution of chitosan–palygorskite composites and removal of aqueous lead by composite beads, Applied Surface Science **353** (2015) 363-375.
- 34. Ministry of Natural Resources and Environment QCVN 40:2021/BTNMT National Technical Regulation on Industrial Wastewater, 2021.