

**INFLUENCE OF ACTIVATORS ON SPENT COFFEE GROUNDS AS BIOSORBENT FOR
CHROMIUM**

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Abstract

Global production of Cr (VI) can reach 44 million metric tons annually, of which 49% is released into the environment. Developments in the industry are to blame for this. There are numerous ways to defend against the damaging impact that heavy metals have on the environment. The presence of Cr (VI) metal causes environmental problems because it can endanger the physical and ecosystem balance of aquatic fauna in river flows. Exposure to Cr (VI) causes health problems such as liver, lung and kidney damage. Adsorption is a straightforward, affordable, and user-friendly technique. The adsorbent utilized is derived from biomass waste, specifically SCG, but its potential as an adsorbent still needs to be developed. The purpose of this work was to examine the impact of activators on activated SCG and its capacity to adsorb Cr (VI) metal. Nitric acid and Bromide acid activators were used to activate 25 g of SCG for 1, 2, and 3 hours. Adsorbent to activator ratios are 1:4, 1:5, and 1:6. Cr (VI) solution was started at a concentration of 100 mg/L, and the adsorption process was stirred at a rate of 300 rpm. In the adsorption process, a ratio of 1:6 is best, along with the best activator, which is HNO₃, solution pH 4, contact time of 120 minutes, and initial solution concentration of 20 mg/L. OH is the major functional group in all adsorbents.

Keywords: Cr (VI) removal, nitric acid activator, bromide acid activator, spent coffee grounds bio-waste

Article Highlights

- Characteristic Adsorbent of *Spent Coffee Ground* (SCG)
- Determination of the best activator for iodine absorption
- Determination of pH of Cr Solution
- Determination of contact time against the percentage of removal
- Determination of concentration to the percentage of Cr (VI) removal

Introduction

Wastewater containing heavy metals, such as Cr (VI) metal, which is a source of environmental contamination, is produced by mining, electrical equipment, leather tanning, and electroplating companies, or so-called anthropogenic activities [1]. Because heavy metals cannot break down, they will be hazardous if they contaminate water. The overall annual output of chromium is 44 million metric tons, of which 49% is generated in nations including Finland, Brazil, Zimbabwe, Kazakhstan, India, South Africa, Turkey, and Zimbabwe. Additionally, more than 170.000 tons of Cr (VI) are released into the environment annually [2,3].

The development of industrialization, urbanization and globalization causes water pollution. Polluted water contains Cr (VI) metal. Cr (VI) metal is a toxic metal that is easily found in river flows. The presence of Cr (VI) metal causes environmental problems because it can endanger the physical and ecosystem balance of aquatic fauna in river flows [4,5]. Long-term exposure to high concentrations of Cr (VI) triggers liver, lung and kidney damage. Meanwhile, short-term exposure to Cr (VI) causes skin irritation. The maximum tolerable concentration of Cr (VI) set by the US Protection Agency (EPA) is 100 mg/L [6,7].

Certain heavy metal species are present in soil, water, and air streams. These species include Pb, Cu, Cd, Hg, As, Ni, and Cr. This is a result of rapid industrial development and poses a risk to human health as well as the environment at the moment [8,9]. The adsorption process is one of many strategies that can be employed to guard against the damaging effects of heavy metals on the environment. In theory, this strategy is straightforward, affordable, and simple to implement [10].

Research is currently focused on using biomass waste, such as potato skins [11], husk lathyrus sativus [12], corncob [13], and garlic straw [14], to create a bio-adsorbent. Though coffee is the second most significant commodity in the world and the largest agricultural product after petroleum [15], the use of SCG, one of the biomass wastes, as an adsorbent is still neglected [16].

Spent coffee grounds SCG is the residue left over after brewing coffee grinds [17]. If not properly treated, SCG frequently ends up as waste that pollutes the environment. Compared to the process, which requires high working temperatures, processing SCG chemically as an adsorbent with an activator has a number of advantages, including direct processing without treatment, operating at ambient temperature, and using less energy [18].

The selectivity and adsorption affinity of SCG are lower, and regeneration is inefficient, this is due to the complexity of the polymer contained in SCG. However, several modification methods, such as physical, mechanical, and chemical make SCG more efficient in the adsorption process. Therefore, the primary objective of this study was to improve the efficacy of modified SCG for Cr (VI) adsorption by altering the type of activator, adjusting the activator ratio, and varying the activation time. In this research, SCG will be activated with a solution of nitric acid and bromide acid. The use of nitric acid and bromic acid in this research was to activate SCG by opening the pores of SCG so that when used to absorb Cr (VI) metal SCG was able to absorb it optimally.

Experiment

Preparation and Characterization of Spent Coffee Ground (SCG)

A total of 2 kg of spent coffee grounds SCG was obtained from Cafeteria Jl. Karya Waisata, Medan Johor, North Sumatra. The SCG that has been collected is then washed using water that has been heated to a temperature of 100 °C, then the SCG is rinsed with clean water. Next, the SCG was dried in an oven at 55 °C for 24 hours. To make a synthetic solution of Cr (VI) dissolve 0.283 g of Potassium dichromate ($K_2Cr_2O_7$) (Pudak. P.a \geq 99.8%), Nitric Acid (65% Emsure), and Bromic Acid (48% Chemie) were used as activators for adsorbent activation using the Batch technique. 1.000 ml of synthetic Cr (VI) solution.

The purity of all the substances utilized is analytical. Fourier Transform Infra Red (FTIR) is used to identify functional groups contained in the adsorbent material. FTIR wave readings are carried out in the middle spectrum region (mid infrared) in the wavelength range 400 – 4000 cm^{-1} . The results of the FTIR test are in the form of a graph between the wavelength (λ) on the x-axis and the amount of light reflected or the percentage (%) transmittance on the y-axis. FTIR test results are analyzed by looking at specific peaks at certain wavelengths. Each specific peak indicates a functional type in the adsorbent compound. SEM (Scanning Electron Microscope) analysis was carried out to determine the surface structure and particle size of each adsorbent. The SEM tool used was JSM-6510 LA, 20 kV 57 PA. The iodine number was carried out to determine the ability of each adsorbent that had been activated by nitric acid and bromide acid to absorb Cr (VI) metal where KI solution was used as an iodine solvent. To determine the iodine concentration, the iodometric titration method is used. The iodine number was measured for both the pre and post activation states of SCG.

Activation Procedure

Distilled water was used three times to get rid of contaminants that stuck to the SCG collected from the café. Next, the SCG is dried for 24 hours at a steady weight in an oven (Memmert, UF110) set to 55 °C. Following the process of drying, The SCG is activated with an activator of Nitric acid dan Bromide acid 0,1 N, activation time of 1, 2, and 3 hours, and an activator to adsorbent ratio of 1:4, 1:5, and 1: 6. After that, the treated adsorbent was dried for two hours at 110 °C using Whatman No. 40 filter paper to remove it from the acid solution and wash it with distilled water until the pH was neutral [19].

Adsorption Experiment

The adsorbent utilized in the adsorption procedure was activated using inorganic acids, and the adsorption test was conducted at room temperature using the batch method. In a 250 ml glass beaker, up to 25 g of adsorbent is combined with a synthetic Cr (VI) solution. A hotplate magnetic stirrer 79-1 was used to stir the mixture under adsorption working parameters of 300 rpm stirring, pH 1–5, and 60–140 minutes of contact time. After filtering the mixture, an atomic adsorption spectrometer (AAS-7000) was used to measure the concentration of the Cr (VI) synthesis solution both before and after adsorption. The determination of Cr (VI) removal is calculated using the following equation [17]:

$$\% \text{ Removal} = \frac{C_i - C_e}{C_i} \times 100\% \quad (1)$$

Where C_i = initial concentration of the solution Cr (VI) (mg/L)

C_e = The equilibrium concentration of the solution Cr (VI) (mg/L)

Results and Discussion

Adsorbent Characteristics

Pore structure analysis using *scanning electron microscope* (SEM)

Figure 1 (a), (b) shows the findings of the SEM analysis for SCG, which was activated using inorganic acids like Nitric acid and Bromide acid. The analysis's findings show that there has been a shape change, with the surface of SCG showing a tendency to have large holes with a uniformly rough texture. It can be believed that the activator from strong acids in the activation process can facilitate the release of contaminants from the SCG material and facilitate the dehydration process, hence facilitating the formation of bigger holes.

Figure 1

Surface functional group analysis of SCG using Fourier Transform Infra-Red (FTIR)

FTIR is employed in the absorption process to identify the adsorbent's functional groups that can interact with the adsorbate [20].

Figure 2.

FTIR spectrum of SCG activated using an activator Bromide acid, and Nitric acid can be seen in Figure 2, the results of the *Infra-Red* (IR) analysis produce the broadest absorption peaks with a spectrum value of 3315.63 cm^{-1} for activator Bromide acid, and activator Nitric acid as big 3317.78 cm^{-1} as well as indicated by the presence of compounds O-H (Hydrogen bonds, alcohols, and phenols). The presence of compound elements C-H (alkanes) for activator Bromide acid and Nitric acid identified at the adsorption peak $2926,01\text{ cm}^{-1}$, adsorption peak $2345,44\text{ cm}^{-1}$ identified compounds C = N that is a triple bond.

In the process of activating SCG with an activator, Bromide acid and Nitric acid were identified to form bonds C = O at the adsorption peak 2058.05 cm^{-1} and 1645.28 cm^{-1} for activator Bromide acid and to Nitric acid 2061.90 cm^{-1} , 1724.36 cm^{-1} 1637.56 cm^{-1} . From the analysis results FTIR from bond strain C=O identified can be associated with amino acids and derivatives of xanthene in the form of caffeine and carboxylic acids from pectin, esters, and aldehydes, which in the adsorption process can participate [18].

The existence of aromatic ring compounds (C=C) was discovered at the adsorption peak 1369.46 cm^{-1} for activator Bromide acid and 1367.53 cm^{-1} for activator Nitric acid, which indicated compounds C-H bending. The amount of Bromide acid is 1527.62 cm^{-1} , and Nitric acid is 1533.41 cm^{-1} . The molecules C-O (carboxyl) detected by activator Bromide acid have an adsorption peak of 1056.99 cm^{-1} .

The functional groups of SCG were activated using inorganic acids, and the resulting FTIR analysis of these groups was utilized to identify the compound elements that the SCG contained, in which the identified compound elements showed that the SCG contained C=N (triple bond), OH, C-H (alkanes), C=O, aromatic ring (C=C), C-H bending, C-O (carboxyl). In addition, with different and increasing OH number intensities in the activated adsorbent Bromide acid and Nitric acid, wherein the adsorption process, the OH group is an ideal active site, and at the same time, indicates that the resulting adsorbent is negatively charged. The research results obtained are as follows per Imessaoudene et al. [21] by using SCG in adsorbing cobalt.

The activator ability to adsorb Iodine

The Iodine adsorption test is used to determine the adsorption capacity and quality of adsorbent in adsorbing the adsorbate using the iodimetric titration method, where the size or smallness of the absorbed amount of iodine serves as an indicator.

Figure 3

SCG can absorb iodine because it contains OH compounds and when SCG is activated using nitric acid and bromide acid, the intensity of OH compounds in SCG as an adsorbent continues to increase, where the OH group becomes an ideal active site in the adsorption process of SCG against iodine. From Figure 3, it can be seen that the adsorption value of Iodine differences from each adsorbent, this is based on the assumption that difference in the ability of solutions or activators to facilitate the pyrolytic decomposition process for the formation of structures related to pores and the surface area of the adsorbent. The adsorption capacity of Iodine can be greatly impacted by hydration and pyrolytic breakdown that occur in the adsorbent material, as reported by Feng et al. [22]. The surface area of the adsorbent is also related to the ability of each activator to increase the porosity characteristics of the adsorbent so that the iodine adsorption capacity increases significantly [23].

Determination of the best activator

The adsorption atom spectrometer (AAS-7000) can be used to examine the beginning and final concentrations of the Cr (VI) solution. 25 ml of Cr (VI) solution at a concentration of 100 mg/L, 60 minutes of contact time, and 300 rpm stirring rate were utilized in the adsorption procedure.

Figure 4

That there is a considerable variation in the percentage of each adsorbent activated with inorganic acids; Bromide acid and Nitric acid have the highest percentages of elimination Cr (VI) at 86.23% and 86.72%, respectively. This is so that the resultant pores and surface area become more open, which impacts adsorption, and the activating ingredient of the inorganic acid utilized can volatile compounds and remove adhering impurities or metal linked to the adsorbent. [22,23].

Effect of pH on Cr (VI) removal

The force of attraction between the adsorbent and the adsorbate is a mechanism of adsorption. The pH variation used in this experiment is 1-5. This aims to determine the best pH conditions for the adsorption of Cr (VI) using an adsorbent activated using Bromide acid and Nitric acid. Where the concentration of the solution is 100 mg/L, the adsorbent dose is 25 g, the contact time is 60 minutes, and the stirring rate is 300 rpm.

Figure 5

Figure 5 shows the removal of Cr (VI) using an adsorbent that has been activated with inorganic acids (Bromide acid and Nitric acid). The maximum removal of Cr (VI) is at pH 4 with a removal value of 98.85% for Nitric acid and 98.37% for Bromide acid; then, by increasing the pH value to 5 for each adsorbent, the percentage of Cr (VI)

removal decreased, which was due to the pH being in an acidic state because when Cr (VI) came into contact with materials containing lignocellulosic it could reduce Cr (VI) to Cr (III), where at low pH the reduction of chromium is a reaction that can bind protons so that if the spent coffee grounds used as an adsorbent can reduce Cr (VI) to Cr (III) then it will be more profitable to adsorb Cr (VI) metal in a low pH atmosphere when compared to high pH [24]. Maximum Cr (VI) removal efficiency can be achieved at low pH due to the presence of various forms of chromium as a function of pH and at the SCG surface charge or zero charge point [25].

Effect of contact time on Cr (VI) removal

Another crucial factor in the adsorption process is the contact time, which is utilized to calculate the ideal mixing [26]. The time variable (60–140 minutes), the adsorbent weight (25 g/L), the initial Cr (VI) concentration (100 mg/L), pH 4 (obtained from earlier investigations), and the stirring rate (300 rpm) were the working parameters.

Figure 6

With an optimal contact time of 120 minutes, the maximum percentage of Cr (VI) removal obtained was 97.87% for adsorbents activated using Nitric acid and 94.88% for adsorbents activated with Bromide acid. SCG, as an adsorbent, demonstrated a significant increase in the percentage of removal as the contact time increased. This is due to the fact that a large number of active sites will be useful in the chromate ion adsorption process, as the active sites will be gradually used up as contact time is added [20].

Effect of initial concentration of Cr (VI) on the percentage removal

The operating conditions used in the experiment to determine the concentration of Cr (VI) solution to the percentage of Cr (VI) removal were those that had been obtained from earlier experiments. These conditions included a 120-minute contact time, an adsorbent weight of 25 g/l, a pH of 4 solution, and a stirring rate of 300 rpm. The Cr (VI) solution employed in this experiment had concentration variations of 20, 50, 80, 110, and 140 mg/L.

Figure 7

As the solution's concentration increased, the percentage of removal Cr (VI) dropped according to the concentration data. It's depicted in Figure 7. where 20 mg/L was the ideal concentration for adsorbents activating with Nitric acid and Bromide acid. This is because the availability of a larger surface area of the adsorbent at low concentrations might accelerate the rate of adsorption [27], whilst the percentage of removal is low at higher concentrations. Ultimately, the sites undergo saturation, allowing for the maximal adsorption of the majority of the metal ions [28].

Conclusion

In this study, we investigated the ability of SCG from biomass waste as an adsorbent to absorb Cr (VI) as a pollutant. The effectiveness of nitric acid and bromic acid as SCG activators was also investigated. SCG was initially activated with nitric acid and bromide acid for three hours. The ability of SCG activated with nitric acid to provide the best iodine adsorption results by showing a removal percentage of 88.92% with an adsorbent to activator ratio of 1:6 with an adsorption value of 234.76 mg/g. Based on the SEM examination results, the adsorbent activated with Nitric Acid had a larger surface texture and more cavities compared to the adsorbent activated with Bromic Acid. The most dominant functional group of the two adsorbents is the OH group, and in

testing the adsorption process the best operating conditions were determined, namely solution pH 4, contact time 120 minutes, and solution concentration 20 mg/L. SCG is used as an adsorbent because it is easy to obtain because it is biomass waste, however the use of SCG as an adsorbent requires a further activation process to increase the absorption percentage, so it has not been used more widely in waste water treatment processes. The application of SCG-based adsorbents in wastewater treatment has challenges because SCG adsorbents require the use of strong acid solutions such as nitric acid and bromide acid which are not safe and environmentally friendly. The use of SCG adsorbent without activation provides a small adsorption percentage compared to that activated by a strong acid solution. Potential limitations or obstacles in this research are the use of strong acid as an activator which is not environmentally friendly, so an alternative activator which is more environmentally friendly or an adsorbent of natural origin is needed which has a higher percentage of absorption without activation. Future potential or findings that are in line with the use of SCG are that SCG has been widely used to absorb contaminants in the form of dyes, lead metal and Cr (III) metal, active carbon precursors, and as compost.

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Figure caption

Figure 1. SEM micrographs of the surface morphology of SCG activated with (a) nitric acid, and (b) bromide acid

Figure 2. FTIR spectra of activated and non-activated SCG

Figure 3. The activator's ability to absorb Iodine

Figure 4. Uptake (percentage of removal) of Cr (VI) by investigated materials

Figure 5. The influence of working pH on Cr (VI) removal

Figure 6. The influence of contact time between adsorbent and pollutant on Cr (VI) adsorption

Figure 7. The influence of the initial concentration of Cr (VI) on the percentage of its removal

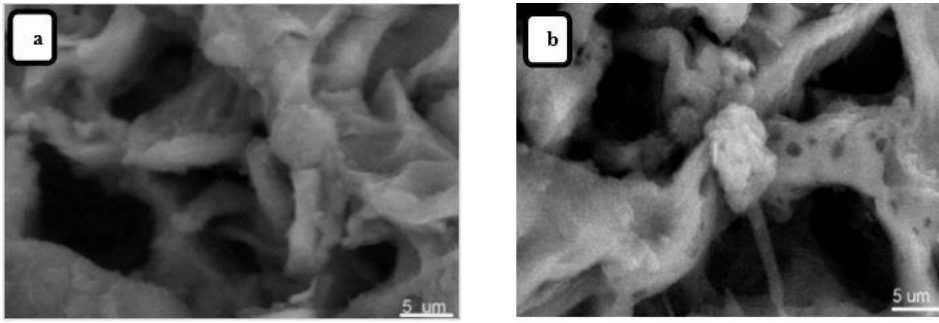


Figure 1.

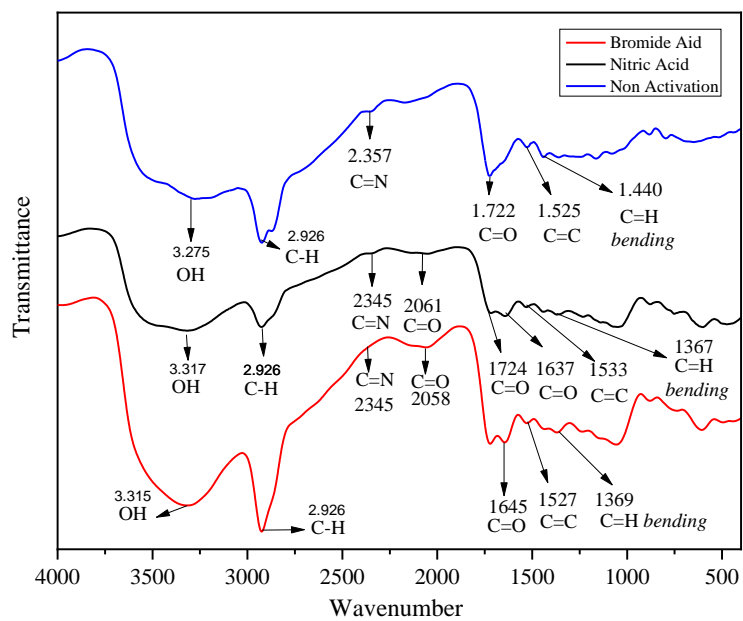


Figure 2.

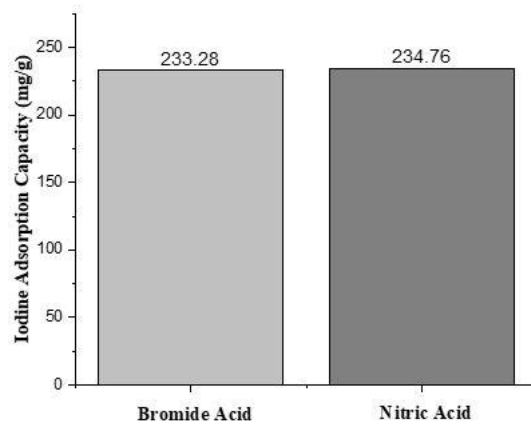


Figure 3.

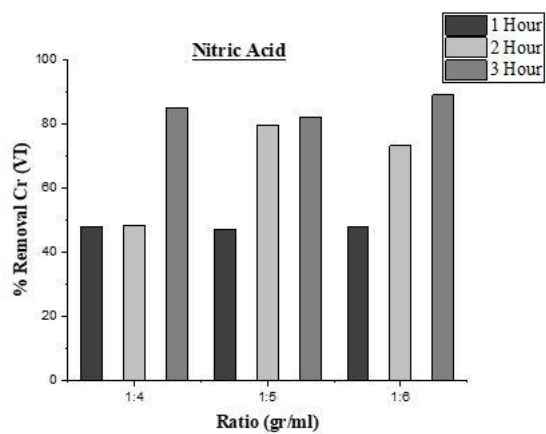
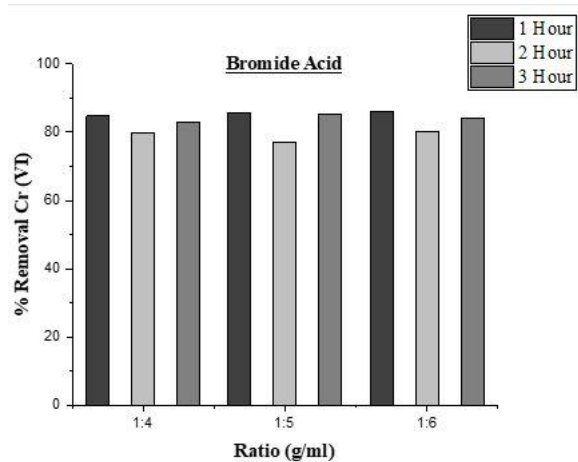


Figure 4.

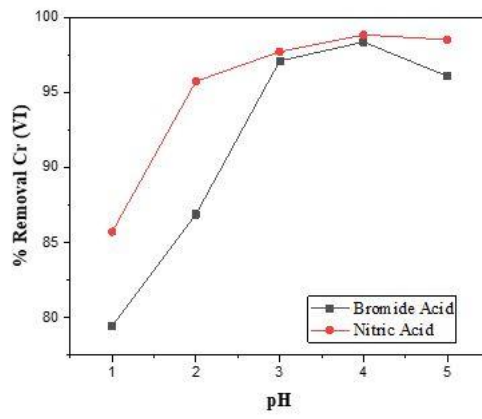


Figure 5.

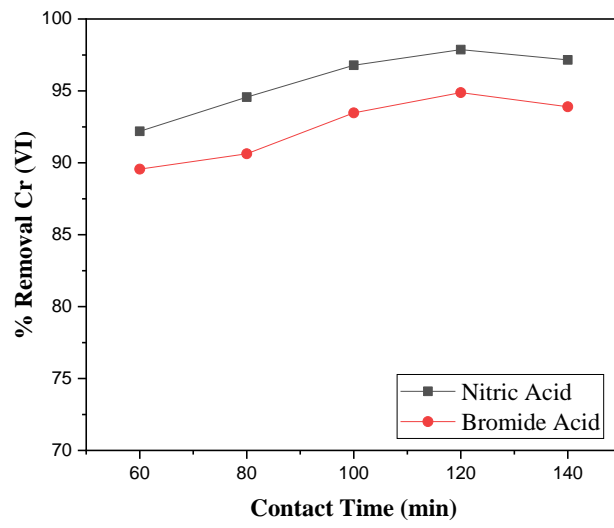


Figure 6.

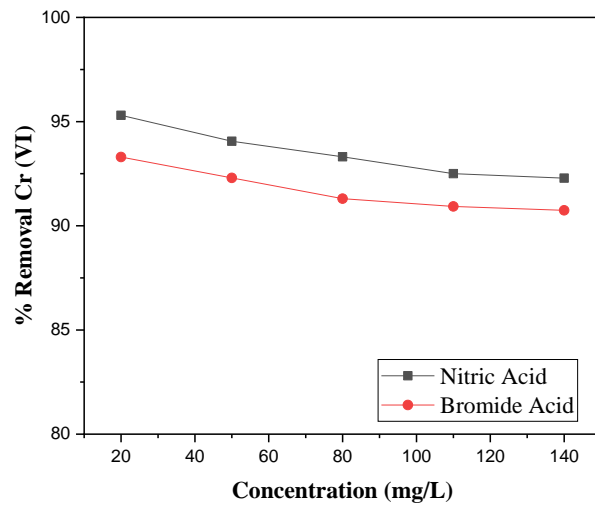


Figure 7.