Synthesis of Reduced Graphene Oxide-Bentonite Composite and Its Application as a Lead(II) Ion Adsorbent

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Received: July 28, 2022
Accepted: December 4, 2022

DOI: 10.22146/ijc.67993

Abstract: *The use of reduced graphene oxide (rGO) as an adsorbent has challenges to overcome. Although rGO has a large surface area, its solubility in water is very low. In this study, bentonite is added to reduce the use of rGO mass and increase the dispersibility of the adsorbent. The rGO-bentonite (rGOB) was characterized by XRD, FTIR, SEM-EDX, and XRF. The adsorption activity was tested in a Pb ion solution, derived from AAS. The XRD pattern of GO, rGO, and rGOB of* 2θ *were observed at 10.90°, 24.88°, and 26.66°, respectively. The FTIR spectrum showed that GO has C=C, C-O, C=O, and O-H, while in rGO, C=O disappears, and there was a significant decrease in the O-H and C-O peaks. The rGOB has identical spectra with rGO and yet has an additional peak from bentonite O-Si-O. The GO and rGO form agglomerate while rGOB looks more dispersed. The C/O ratio increases from GO to rGO because of the reduction process. The bentonite is Ca-bentonite with main components* Al_2O_3*,* SiO_2*, and CaO. The results showed that the rGOB composite could reduce the use of rGO by up to 80% and have an adsorption performance similar to rGO with an adsorption capacity of 217 mg/g.*

Keywords: *adsorption; bentonite; lead; reduced graphene oxide; reduced graphene oxide-bentonite*

■ INTRODUCTION

Lead (Pb) is a toxic metal that leads to various environmental problems that need removal from wastewater. Reduced graphene oxide (rGO) is a material that has the potential as an adsorbent for Pb ion due to its large surface area but has poor dispersibility and is relatively difficult to produce. Lead is one of the most dangerous heavy metals that can cause various environmental problems. The agency for toxic substances and disease registry (ATSDR) even placed Pb in second place on the 2019 substance priority list regarding its amount in the environment, potential human exposure, and potential threats to human health [1]. The extensive use of lead in various industrial fields causes pollution by lead to be unavoidable, so more efforts are needed to reduce lead pollutants in industrial waste before entering the environment. Different methods have been used to reduce the Pb concentration in industrial wastewater, such as chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation and flocculation, flotation, and electrochemistry. However, adsorption is the most effective and economical process because of its ease of design and operation [2]. Many materials have been tested as Pb(II) adsorbents [3-5]. Still, most of them cannot be used effectively because of their low adsorption capacity, long equilibrium time, or high prices, so various materials are continuously being developed to get better adsorbents.

Because of its enormous surface area, rGO is a promising material as a Pb(II) adsorbent. However, in an aqueous solution, rGO presents in an aggregate [6], reducing its adsorption capacity. Besides, the rGO material is quite challenging to be produced, leading to its use as an adsorbent on a large scale becoming ineffective. Therefore, the rGO will be composited with bentonite to reduce its use in the adsorbent. High dispersibility bentonite [7] is expected to increase the dispersibility of rGO. Bentonite was chosen because this material has a high abundance, relatively low prices, and is environmentally friendly [8].

Furthermore, compared to many other natural materials, bentonite has a large surface area and cation exchange capacity [9]. Therefore, the bentonite in the adsorbent would contribute to adsorbing Pb(II) and increase the overall adsorbent ability. So far, there is no publication found related to the application of reduced graphene oxide-bentonite (rGOB) as a Pb adsorbent.

In this work, graphene oxide was prepared from commercial synthetic graphite powder using a modified Hummer method which will then be reduced using hydrazine to form rGO [10]. Subsequently, an rGOB composite was made by combining the rGO and bentonite through a radical reaction [11]. The rGOB composites will be synthesized with two rGO/bentonite ratio variations to determine a better adsorbent composition. The rGOB composites were then characterized using XRD, FTIR, SEM-EDX, and XRF. The adsorption capability of synthesized material on Pb(II) solution that uses a batch adsorption system was evaluated using AAS.

■ EXPERIMENTAL SECTION

Materials

Ammonium persulfate ($(NH_4)_2S_2O_8$) (98%), commercial natural bentonite, commercial synthetic graphite (98.6%), demineralized water (H_2O), ethylene glycol ($C_2H_6O_2$) (99.5%), hydrazine (N_2H_4) (98% purity), hydrogen peroxide (H_2O_2) (30%), lead (Pb) stock solution (1000 ppm concentration), nitric acid (HNO_3) (65%), phosphoric acid (H_3PO_4) (85%), potassium permanganate ($KMnO_4$) (99.0%), sodium bisulfate ($NaHSO_4$) (99.0%), sodium hydroxide (NaOH) (98.0%), sulfuric acid (H_2SO_4) (95–97%). All substances are derived from Merck.

Procedure

Synthesis of graphene oxide

Graphene oxide was prepared using synthetic graphite obtained commercially based on the Hummer method modified by Husnah et al. [10]. A 2.5 g of graphite powder was added into a beaker containing 57.5 mL H_2SO_4/H_3PO_4 (9:1) in an ice bath. The mixture was stirred until the temperature reached ± 10 °C. Next, 7.5 g of $KMnO_4$ was slowly added to the suspension while stirring, and the temperature was kept below 20 °C. The suspension was then heated to 50 °C while stirring for 40 min.

Furthermore, the suspension was slowly poured into 125 mL of demineralized water. The oxidation process was stopped by adding 2.5 mL hydrogen peroxide 30%. The suspension was then filtered through a Whatman paper, and the solid obtained was washed with demineralized water. The graphene oxide obtained was dried at 60 °C for 12 h.

Synthesis of reduced graphene oxide

Reduced graphene oxide was prepared by reducing GO using hydrazine via microwave heating by following the method developed by Husnah et al. [10]. Graphene oxide (2 g) was dispersed in 100 mL ethylene glycol with 2 h of sonication, followed by an hour of magnetic stirring. Then, 2 mL of hydrazine (N_2H_4) is added dropwise while stirring. The reduction process was completed by introducing the suspension into microwave heating at 100 °C for 20 min. The suspension was then filtered and washed with demineralized water. The reduced graphene oxide was dried at 60 °C for 12 h before being grounded into a powder and then sieved (325 mesh).

Synthesis of reduced graphene oxide-bentonite composites

Reduced graphene oxide-bentonite (rGOB) composites were prepared using a persulfate/bisulfate initiator [11]. The rGO suspension was prepared by dispersing 0.4 g of rGO in 150 mL of demineralized water after 2 h of sonication. At the same time, the rGOB suspension was prepared by dispersing an amount of rGO with a varied amount of bentonite (2 and 4 wt.%) in 100 mL demineralized water for 2 h stirring. After that, 16 mL of 40% NaOH aqueous solution, 16 mL of 1% $(NH_4)_2S_2O_8$, and 16 mL of 1% $NaHSO_4$ were added to the suspension and heated at 65 °C for 2 h while stirring. It was then cooled at room temperature before being filtered by a Whatman paper. The rGOB solid (rGOB (1:2) and rGOB (1:4)) obtained was then washed with demineralized water before being dried at 60 °C for 12 h. It was grounded into a powder and sieved (325 mesh).

Characterization of materials

The X-ray powder diffraction data were collected with X-ray Diffraction Spectrometer X'Pert Powder PW 30/40 using a Cu-sealed tube (CuKα X-rays of 0.15406 nm, operating at 40 kV and 30 mA). Each system was measured in the scattering 2θ range of 5° to 100° with a step of 0.026° and scan step time of 7.14 s. Spectra of dried graphite, bentonite, graphene oxide, reduced graphene oxide, and reduced graphene oxide-bentonite obtained by Fourier Transform Infrared Spectrometer Nicolet Avatar 360 IR, pellet KBr, from 4000–400 cm^{-1} of the spectral region, and functional groups of materials can be observed. The morphology of the synthesized sample was observed by SEM JSM-6510 LA, using Au coating. The composition of bentonite was measured using XRF Rigaku-NexQC+QuanTEX.

Pb(II) adsorption

A total of 0.01 g of rGO, rGOB (1:2), or rGOB (1:4) was added to 50 mL of 50 ppm of Pb (II) solution (pH 1). The solution was then stirred with a magnetic stirrer for 60 min at room temperature (26 ± 2 °C). After that, the solution was filtered with Whatman filter paper, and the obtained filtrate was measured. The adsorption test was carried out three times for each adsorbent. Pb has measured the solution using an atomic absorption spectrometer graphite furnace 240Z AA Agilent Technologies. The source of the Pb hollow lamp is 217 nm, slit width 1.0 nm, 20–60 μg/L range of standard solution. The removal efficiency (R) and adsorption capacity (Q) using Eq. (1) and (2).

$$R = \frac{C_i - C_f}{C_i} \times 100\% \qquad (1)$$

$$Q = \frac{(C_i - C_f) \times V}{W} \qquad (2)$$

where C_i = initial concentration of Pb solution (mg/L), C_f = final concentration of Pb solution (mg/L), V = volume of solution (L), and W = mass of adsorbent (g)

RESULTS AND DISCUSSION

Graphene oxide is prepared using synthetic graphite obtained commercially *via* the modified Hummer method by Husnah et al. [10]. The temperature was kept below 20 °C when graphite contacted H_2SO_4/H_3PO_4 and $KMnO_4$ to prevent explosions because the reaction between $KMnO_4$ and H_2SO_4 would produce Mn_2O_7 which was very reactive and could cause an explosion at temperatures above 55 °C [12]. Graphite will react with H_2SO_4 in the presence of $KMnO_4$ to produce intercalated graphite [13]. The temperature escalation in the reaction causes more oxygen functional groups to be formed, and the oxidizers begin to enter the interlayer, which causes an increase in the graphite interlayer distance [14]. H_3PO_4 prevents excessive oxidation, which causes defects in the graphene layer [15]. The oxidation process was quenched by adding 30% H_2O_2, which will reduce the remaining $KMnO_4$ to $MnSO_4$ [16].

Reduced graphene oxide was made by reducing GO using hydrazine with the assistance of a microwave [10]. Graphene oxide is suspended in ethylene glycol using sonication to reduce particle agglomeration. Besides that, it can weaken the Van der Waals bonds between the graphene layers so that GO will be exfoliated [17]. Hydrazine is added to the suspension to reduce the oxygen functional group on GO.

The GO reduction process is completed by heating GO using a microwave at a temperature of 100 °C. The oxygen functional group in GO will be reduced thermally during heating. The suspension was then filtered, and the rGO obtained was washed with demineralized water, dried at 60 °C for 12 h, then ground into powder and sieved with a 325-mesh sieve.

The reduced graphene oxide-bentonite composite was prepared using a radical reaction with the help of a persulfate/bisulfate initiator. Suspension of rGO and bentonite were dispersed in demineralized water by a magnetic stirrer in the persulfate/bisulfate redox system. Ammonium persulfate and sodium bisulfate act as initiators and will form free radicals on the bentonite hydroxyl group so that bentonite can form bonds with rGO [11]. Sodium hydroxide was used to increase the pH and initiate the initiation reaction. The reaction begins by heating the suspension at 65 °C while stirring with a magnetic stirrer. At this stage, the initiator will cause the formation of free radicals on some of the bentonite hydroxyl groups, which will then form bonds with rGO [11]. The suspension was then cooled to room temperature to stop the entire reaction process, filtered, and washed with demineralized water at 60 °C for 12 h. The materials used in this research are described in Fig. 1.

XRD Characterization

Graphite, GO, and rGO XRD diffractograms (Fig. 2) have diffraction peaks (002) at 2θ = 26.37° (graphite), 2θ = 10.90° (GO), and 2θ = 24.88° (rGO) which shows the distance between the graphene layers and the 2-dimensional diffraction peaks (10) at 2θ = 42.63° (GO) and 2θ = 43.41° (rGO) which shows the short-range order of the graphene stack [18].

Fig. 2 shows the diffraction patterns, which were processed using OriginPro *via* fitting to the Gaussian function. The diffraction peak (002) was applied to the Bragg equation to calculate the distance between the graphene layers (**d**) and laid into the Scherrer equation with a constant of 0.9 (Eq. (3)) to calculate the average height of the graphene stack (**H**) so that the number of graphene layers (**n**) could be estimated (Eq. (4)). The 2-dimensional diffraction peak (10) was applied into the Scherrer equation with a Warren constant of 1.84 (Eq. (5)) to estimate the mean diameter (**D**) of GO and rGO [18].

$$H = \frac{0.9\lambda}{\beta\cos\theta} \tag{3}$$

$$n = \frac{H}{d} \tag{4}$$

$$D = \frac{1.84\lambda}{\beta\cos\theta} \tag{5}$$

where λ = wavelength (nm), β = full width at half maximum (rad), and θ = angle of light (rad)

Table 1 shows the calculated crystal size of graphite, GO, and rGO. Graphite crystals have a graphene

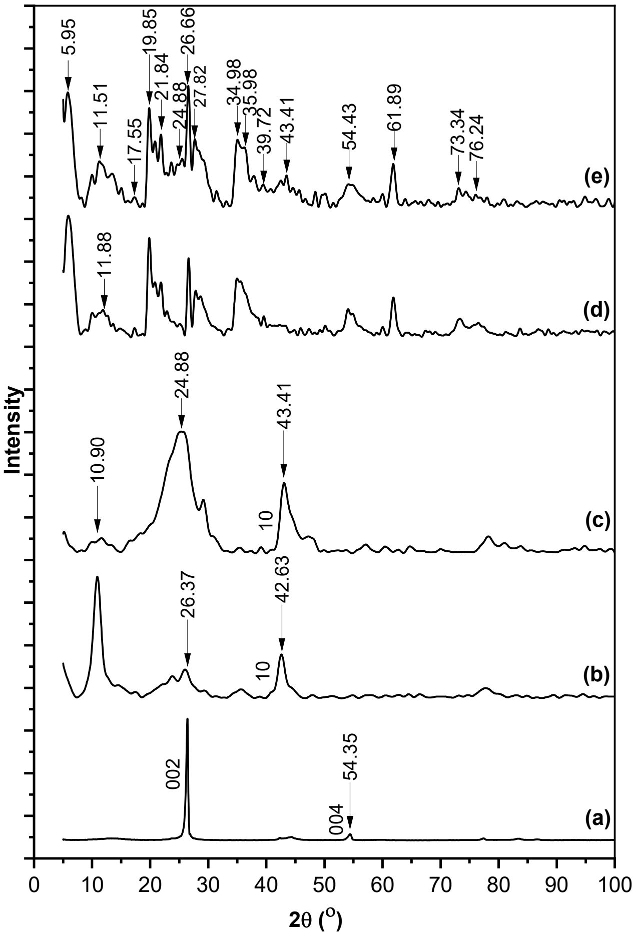


Fig 2. XRD diffractograms of graphite (a), GO (b), rGO (c), bentonite (d), and rGOB (e)

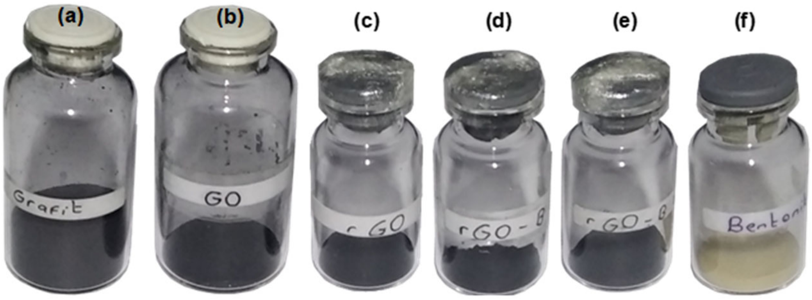


Fig 1. The visualization of samples of graphite (a), GO (b), rGO (c), rGOB (1:2) (d), rGOB (1:4) (e), and bentonite (f)

Table 1. The results of calculating the crystal size of graphite, GO and rGO

	Peak (002)				
	2θ (°)	FWHM (°)	H (nm)	d (nm)	N
Graphite	26.37	0.4258	19.16	0.34	56–57
GO	10.90	1.7597	4.54	0.81	5–6
rGO	24.88	6.2327	1.31	0.36	3–4
	Peak (10)				
	2θ (°)	FWHM (°)	D (nm)		
GO	42.63	1.4920	11.69		
rGO	43.41	2.2971	7.61		

interlayer distance of 0.34 nm and increase to 0.81 nm in GO due to the oxygen functional groups in the graphene interlayer. The graphene interlayer distance at rGO decreases again to 0.36 nm, indicating that GO has been successfully reduced and the structure of the graphene layer has been restored [19]. Besides, the number of graphene stacks was also reduced from 56–57 in graphite to 5–6 in GO and 3–4 in rGO. Based on the calculation results, GO crystals have an average size of 11.69 nm × 4.54 nm, while in rGO, the average size of the crystals decreases to 7.61 nm × 1.31 nm. The smaller the crystal size, the larger the surface area of the crystal, and it will increase its adsorption ability.

The diffractogram of bentonite (Fig. 2(d)) has characteristic peaks at 2θ = 5.95°, 11.88°, 17.55°, 19.85°, 27.82°, 34.98°, 35.98°, 54.43°, 61.89°, 73.24°, 76.24° (montmorillonite), 21.84°, 26.66°, 39.72° (quartz), and 21.84° (cristobalite) [20,21]. On the rGOB diffractogram (Fig. 2(e)), the peaks of 11.88° and 27.82° shifted to 11.51° and 28.44°. Also, there are new peaks at 2θ = 24.88° and 43.41° from the characteristic peaks of rGO.

FTIR Analysis

Fig. 3 shows a broad peak at 3430 cm^{-1} (stretching OH) due to the adsorbed water and peaks at 1630 cm^{-1} and 1550 cm^{-1} (stretching C=C) due to the vibrations of the graphite domain. The peak at 3430 cm^{-1} may appear because the drying process could be better, so water molecules are still trapped in the graphite powder. The intensity of the peak at 3430 cm^{-1} vastly increased, and there are two new peaks at 1712 cm^{-1} (stretching C=O) and 1050 cm^{-1} (stretching C-O) in the GO spectra (Fig. 3(b)), which indicated the presence of many oxygens functional groups after the oxidation process. The new peaks at 2925 cm^{-1} and 2850 cm^{-1} (stretching C-H) showed the presence of CH_2 groups in GO samples. The graphite domain vibrational peak on GO also shifted to 1615 cm^{-1} and 1572 cm^{-1}. At rGO spectra (Fig. 3(c)), the peak intensity at 3430 cm^{-1} and 1050 cm^{-1} decreased significantly, while the peak at 1712 cm^{-1} did not appear, indicating that all carbonyl and carboxylate groups and some hydroxyl and epoxide groups were successfully reduced. The peaks at 2925 cm^{-1} and 2850 cm^{-1} still found on rGO told that the graphite domain frame was not successfully recovered. The vibrational peaks of the graphite domain frame also shifted to 1645 cm^{-1} and 1550 cm^{-1} [22-23].

The FTIR spectra of bentonite (Fig. 3(d)) have a peak at 3450 cm^{-1} (OH stretching) and 1640 cm^{-1} (bending OH) from adsorbed water. The 3450 cm^{-1} peak can come from the OH group on the rGO that failed to reduce and water molecules trapped in bentonite due to the imperfect drying process. Two peaks at 3630 cm^{-1} (OH stretching) and 912 cm^{-1} (bending OH) due to Si-OH in the tetrahedral bentonite layer. Peaks at 1040 cm^{-1} correlated to the stretching of Si-O, while 522 cm^{-1} and 466 cm^{-1} for bending Si-O from Si-O-Si in the tetrahedral layer of bentonite. The peak characteristic of bentonite was also seen at 795 cm^{-1} [20,22,24]. In the rGOB spectra (Fig. 3(e)), the peak intensity at 3630 cm^{-1} and 912 cm^{-1} decreased because some of the hydroxyl groups in bentonite formed bonds with rGO [11]. The peak of rGO characteristics did not appear in the rGOB spectra because the characteristic peaks of bentonite covered it.

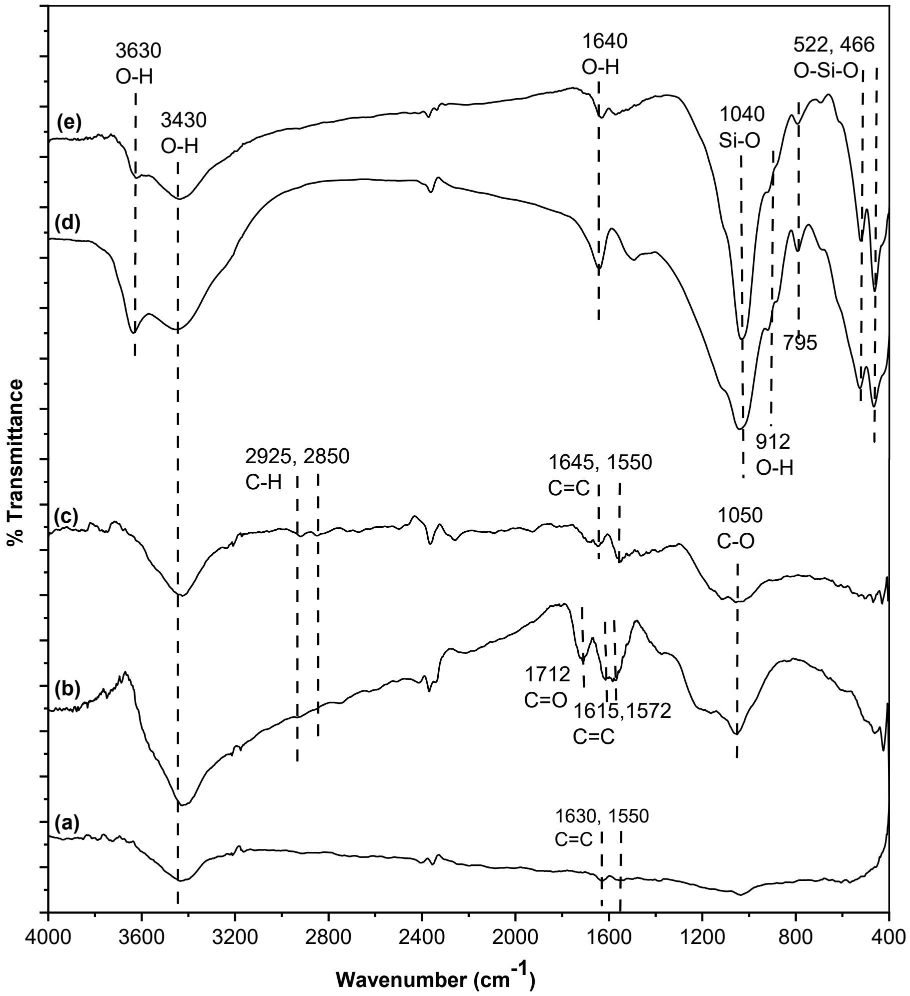


Fig 3. FTIR spectra of graphite (a), GO (b), rGO (c), bentonite (d), and rGOB (e)

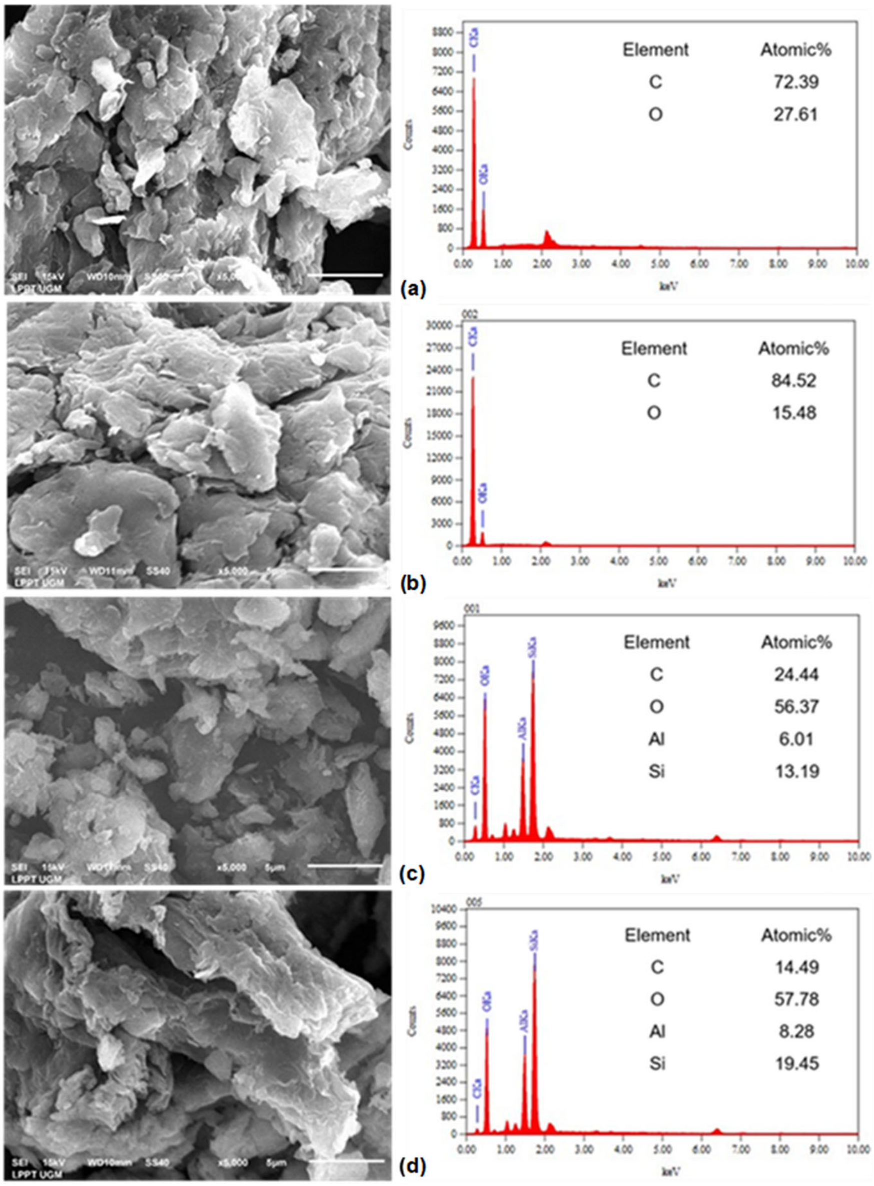
SEM-EDX Analysis

Micrograph SEM (Fig. 4) of GO showed a layered structure with a rough surface and flaking flakes. The presence of these flakes indicates that the graphene surface has been successfully oxidized to GO. The results of the EDX analysis also showed the presence of oxygen atoms as much as 27.61%, which proved that the oxidation process was successful. After being reduced to rGO, the shape looks like small pieces with a wrinkled and folded surface, a characteristic of rGO materials [14,25]. In addition, the results of the EDX analysis (Fig. 4) also showed a decrease in the number of oxygen atoms from 27.61% in GO to 15.48% in rGO, indicating that the reduction process had been successfully carried out.

Both GO and rGO appear to form clumps, which could be due to prolonged heating [14]. The clumping form can cause the adsorption ability of the material to be reduced. However, when rGO was composited with bentonite, it was seen that rGO adhered to the bentonite surface. The EDX results also showed the presence of Si and Al, which are the main components of bentonite. Based on the micrograph, bentonite does not appear to form large clumps, and rGO spreads on the bentonite surface. So that when used in the adsorption process, the material can be evenly dispersed in the solution and has a better adsorption ability.

XRF of Bentonite

Table 2 shows the composition of bentonite XRF determination. The results of the XRF test showed that there was a relatively high content of SiO_2 and Al_2O_3. Both are the main ingredients of bentonite. The presence



(a)

Element	Atomic%
C	72.39
O	27.61

(b)

Element	Atomic%
C	84.52
O	15.48

(c)

Element	Atomic%
C	24.44
O	56.37
Al	6.01
Si	13.19

(d)

Element	Atomic%
C	14.49
O	57.78
Al	8.28
Si	19.45

Fig 4. Micrograph SEM and EDX analysis of GO (a), rGO (b), rGOB 1:2 (c), and rGOB 1:4 (d)

Table 2. Bentonite composition from XRF result

Component	% Mass
Al_2O_3	10.85
SiO_2	63.33
CaO	25.82

of CaO indicates that the bentonite used is Ca-Bentonite. Many studies have been conducted to test the ability of bentonite as an adsorbent for heavy metals due to its abundant availability, relatively low price, environmentally friendly [8], and large surface area and cation exchange capacity [9]. However, the results showed that the adsorption capacity of bentonite to Pb ion was not very high, only 19–85 mg/g [26-28].

Pb(II) Adsorption Activity Test

Table 3 shows the application of synthesized material as an adsorbent for Pb ion. The adsorption test was carried out on a 50 ppm (pH 1) Pb(II) solution with the batch adsorption method. The results showed that the rGO adsorbent had the highest adsorption capacity with an average adsorption capacity of 218 mg/g, followed by rGOB (1:4) of 217 mg/g, and finally, rGOB (1:2) of 216 mg/g. However, the results of the t-test with

Table 3. The results of the adsorption test on the Pb(II) solution

Adsorbent	Pb concentration after adsorption (ppm)	Removal efficiency (%)	Adsorption capacity (mg/g)
rGO	6.688	87	217
	6.537	87	217
	6.129	88	219
Average ± SD		87	218 ± 1.45
rGOB (1:2)	6.459	87	218
	7.452	85	213
	6.586	87	217
Average ± SD		86	216 ± 2.70
rGOB (1:4)	6.872	86	216
	6.316	88	218
	6.757	86	216
Average ± SD		87	217 ± 1.47

Table 4. The adsorption capacity of some adsorbents to Pb(II) at room temperature

Adsorbent Material	pH	Adsorption capacity (mg/g)	Ref.
Activated carbon	7	31–59	[29]
Natural bentonite	5.5	71	[27]
Porous cellulosic	6	52	[30]
Magnetic graphene oxide functionalized cyanopropyl nanocomposite	5	111	[31]
Halloysite nanotube-rich carboxyl carbon	6	184	[32]
Magnetic Fe_3O_4-encapsulated $C_3N_3S_3$ polymer/reduced graphene oxide	6	270	[33]
Reduced graphene oxide-bentonite composite*	1	217	Present work

*Optimization of adsorption conditions has not been carried out

a 95% confidence interval showed that the removal efficiency for each adsorbent did not have a significant difference. The rGOB composite has the same efficiency as rGO, but the rGOB composite (1:2) can reduce the use of rGO by 66%, and even at rGOB (1:4), it can reduce the use of rGO by 80%.

Table 4 shows the comparison of some adsorbents to Pb ions. The rGOB composites can reduce the use of rGO very significantly but still have an equivalent adsorption capability. It is because, in a suspended state, rGO will form an aggregate [6] so that it will significantly reduce its adsorption capacity. The bentonite added to the adsorbent is a highly dispersed material [34]. The rGOB adsorbent produced also has good dispersibility and causes the ability of the rGOB adsorbent not to decrease when compared to the rGO adsorbent. In addition, bentonite is also a heavy metal adsorbent, so it also contributes to the adsorption of Pb(II). The rGOB composites synthesized in this study have a high adsorption ability, so they have the potential to be used as heavy metal adsorbents.

■ CONCLUSION

The reduced graphene oxide-bentonite was successfully synthesized. The diffractogram of XRD shows the identity of GO, rGO, and bentonite. The FTIR spectrum described the functional group of materials qualitatively. The SEM-EDX confirms the morphology and composition of the material. The XRF of bentonite sure the compound in it. The adsorption activity of the materials against Pb ion in the sample shows that the materials can run as an adsorbent well. The resulting rGOB composites can reduce the use of rGO by up to 80%, but they still have an adsorption capability similar to rGO. The rGOB adsorbent can adsorb Pb up to 87% and has an adsorption capacity of 217 mg/g.

■ ACKNOWLEDGMENTS

This work was supported by grants from Mathematics and Natural Sciences Faculty, Universitas Tanjungpura Pontianak, under DIPA UNTAN Grant No. SP DIPA-042.01.2.400955/2019. The authors express great gratitude for that support.

■ AUTHOR CONTRIBUTIONS

Bartholomeus Lavelim conducted the experiment and wrote the manuscript draft, Lia Destiarti concept the methodology and revised the manuscript, Adhitiyawarman wrote and revised the manuscript, and Risya Sasri checked the data accuracy. All authors agreed to the final version of this manuscript.

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