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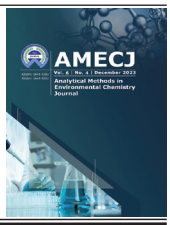

Design of sludge drying package pilot for removal of excess sludge in petrochemical industries: Heavy metals determination in sludge by polarography and atomic absorption spectrometry

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ABSTRACT

In this research, according to the high amount of sludge in a petrochemical company, an iron package type of drying sludge bed was made/designed with carbon steel. Then, the drying sludge pond was filled with layers of sand with different mesh sizes. The excess sludge from the sedimentation pond was passed over this bed, and the amount of sludge removed by the bed was obtained at %96. The values of heavy metal and microbial forms were determined using the proposed method based on activated sludge after wastewater treatment. For the validation process, 10 mL of deionized water (DW) was mixed with 1.0 g of dried sludge with pure nitric acid (2% HNO_3), and then the solid phase was filtered with the Whatman filter (WF). The concentration of heavy metals (As, Cd, Cu, Pb, Hg, Mo, Ni, Co, Se, Zn) in the remaining solution of sludge (mg kg^{-1}) and wastewater (µg L^{-1}) was extracted/ separated based on sulfur-doped graphene oxide adsorbent (SDGO) by solid-phase microextraction procedure (SPME) before being determined by the flame and hydride generation atomic absorption spectrometry (F-AAS; HG-AAS) which had similar range to the polarography analysis. The limit of detection (LOD), linear range (LR) and preconcentration factor (PF) for (As, Hg) and (Cd, Cu, Pb, Mo, Ni, Co, Se, Zn) were obtained (0.016 µg L^{-1}; 3.3 µg L^{-1}), (0.05-10 µg L^{-1}; 10-1000 µg L^{-1}), and 10.0 by HG-AAS and F-AAS, respectively.

1. Introduction

Wastewater treatment is always associated with producing two parts: sewage and sludge. Effluent after secondary treatment is often of favourable quality for discharge into the environment, while sludge requires treatment and stabilization due to its high pollution load. Wastewater treatment concentrates the impurities and pollutants in them and separates them from the liquid phase. The detached part contains a high concentration of contaminants and undesirable substances that must be purified appropriately. This part is generally called sludge. In a wastewater treatment plant, sludge treatment and stabilization facilities are far more sensitive, specialized, and expensive than other units. So, sludge treatment

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and disposal devices usually account for 40 to 60 percent of the construction cost and up to 50 percent of the operation cost of a treatment plant, creating a significant share of the operational problems related to this facility. Based on this, special attention should be paid to the technical and economic optimization of sludge purification and stabilization methods [1]. The main technology in wastewater treatment is removing organic matter by biological oxidation. The final products of this process are new cells (sludge), carbon dioxide, soluble microbial products, and water. The activated sludge process is widely used worldwide in municipal and industrial wastewater treatment. The daily production of excess sludge from the conventional activated sludge process is about 15 to 100 litres per kilogram of BOD_5 removed, which contains more than 95% water [2]. Since the sludge produced as a waste material must continuously be discharged into the environment economically, biomass production is of economic importance. Nowadays, the solutions to minimize excess sludge production in the activated sludge process are becoming very practical. Therefore, it seems necessary to review the methods used to reduce the sludge production from the activated sludge process on an industrial scale [3]. Until now, the main techniques are the aerobic process with anaerobic sedimentation [4], activated sludge process combined with ozonation [5], sludge retention time control and its biological decomposition [6], and high dissolved oxygen process [7] for the management of excess sludge produced in the activated sludge process has been reported. Since the disposal of excess sludge from purification systems in the environment is done either as compost (fertilizer) or as landfill, the presence of heavy metal pollution plays an important and influential role in its disposal because the entry of heavy metals into the soil and the structure of plants, it will eventually appear in the human body through diffusion in water and dust. Heavy metals such as arsenic (skin cancer) [8-9], cadmium (lung cancer) [10-11], copper (kidney and liver failure) [12], lead (destroying the nervous system) [13], mercury (congenital abnormalities) [14-15], molybdenum (hyperactivity and convulsion factor) [16], nickel (cardiovascular abnormalities) [17] and selenium (kidney and liver destruction) [18] which are considered a serious threat to human health. There are many methods for determining and extracting heavy metals from different matrixes. Recently, some adsorbents such as nano graphene oxide modified phenyl methanethiol nanomagnetic composite, Fe3O4-supported naphthalene-1-thiol-functionalized graphene oxide (SH-GO), CysSB/MetSB@MWCNTs, task-specific ionic liquid immobilized on multi-walled carbon nanotubes (TSIL-MWCNTs), functionalized multi-walled carbon nanotubes (F-MWCNTs), MWCNTs@DMP, nitrogen-doped porous graphene adsorbent (NDPG), immobilization of N-acetylcysteine on MWCNTs, thiol modified bimodal mesoporous silica (HS-UVM7), and palladium embedded on the mesoporous silica (Pd-MSN) were used for extraction and determination heavy metals in different matrixes[19-31].

Therefore, in this research, the design and construction of a pilot sludge drying reactor to dispose of the excess sludge of petrochemical industries (methanol) and measure the amount of fecal coliforms, and heavy metals such as cadmium, copper, lead, nickel, cobalt and zinc (Cd, Cu, Pb, Ni, Co, Zn were determined by polarography (VT). Also, after treatment in the resulting sludge, Hg, As, Se, Mo plus Cd, Cu, Pb, Ni, Co, and Zn were determined by F-AAS and HG-AAS.

2. Experimental

2.1. Instrumental

Polarography is an electrolysis technique in which micro-electrodes are performed at a solution's dropping mercury electrode (DME). The polarography device measured the heavy metals (Metrohm model VA Computrace 797, Swiss) by the anodic stripping voltammetry (ASV) mode. The results are achieved as a current–voltage curve (CVC). Polarography or voltammetry technique (VT) determines ion species based on loss or take electrons at the surface of a DME at an optimized potential. Electrode surfaces are used for inorganic and organic compounds. Polarography is used for heavy metal analysis (Cd, Cu, Pb, Ni, Co, Zn) in high sludge concentrations (mg kg^{-1}), but it cannot determine the low concentration of less

than ppm. The Flame atomic absorption spectrometry had more sensitivities (DL<0.1 mmol L^{-1}) compared to polarography (DL>0.1 mmol L^{-1}). In analytical applications, the alternating current (AC) mode has more sensitivities than the direct current (DC) polarography, but it is better to use the FAAS for a low detection limit. In this work, we used polarography/ VT and F-AAS /HG-AAS for high and low values of heavy metals in sludge. The cold vapor-atomic absorption spectrometer (CV-AAS) was used for trace determination of mercury in the water samples (HG-3000, GBC, Aus). The $NaBH_4$ reagents and a reaction loop were used for mercury determination by CV-AAS. The linear ranges (LR) and the detection limit (LOD) of mercury were obtained between 1-60 µg L^{-1} and 0.25 µg L^{-1}, respectively, by open quartz cell of CV-AAS. The wavelength, the current lamp and the slit of mercury HCL were tuned at 253.7 nm, 3 mA and 0.5 nm, respectively, by AAS (peak area). The HG-AAS was also used for arsenic determination in water samples. Other heavy metals such as Cd, Cu, Pb, Mo, Ni, Se, Co and Zn were determined by flame atomic absorption spectrometer (F-AAS, GBC 932 plus, Autosampler, Air/Acetylene). The mean LOD and LR for Cd, Cu, Pb, Mo, Ni, Se, and Zn were obtained from 50-100 µg L^{-1} and 0.1-10 mg L^{-1}, respectively. A pH meter determined the sample pH (Metrohm AG 744, Switzerland).

2.2. Reagents and Materials

The different layers used in the designed bed consist of sand with different meshes, which are very economical. All reagents, such as nitric acid (Sigma, CAS No.: 7697-37-2, 65%) and sodium hydroxide, were purchased from Sigma and Merck (Germany). The standard solutions of arsenic, cadmium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc (As, Cd, Cu, Pb, Hg, Mo, Ni, Co, Se, Zn) were purchased from Sigma, Germany. The different standard solutions of heavy metals were prepared by amounts of metal salt as 1000 mg L^{-1} solution by dissolving in HNO_3 (2%). The sample pH was adjusted using proper buffer reagents of sodium acetate (CAS No.: 6131-90-4, CH_3COO-Na/CH_3COOH) for pH 3 to 7.5. Pure GO (CAS No.: 1034343, CxHyOz) prepared from Sigma Aldrich, Germany. Sodium sulphite (CAS No.: 7757-83-7, Na_2S) was purchased from Merck, Germany.

2.3. Synthesis of sulfur-doped graphene oxide

The pure GO was prepared from Sigma, Germany. First, 5.0 mg of pure GO was dispersed in 10 mL of DW and was sonicated for 30 min as suspension material before adding 1.5 mL of Na_2S (2%). The mixture was shaken for 85 minutes at 95 °C, and S-doped reduced graphene oxide was produced (SDGO). Then, the SDGO adsorbent was cooled and separated (25°C) by centrifuging. The final product was washed with DW many times and separated by the Whatman filter. After drying for 2 hours in the oven (70°C), the adsorbent is used for further work (Fig.1).

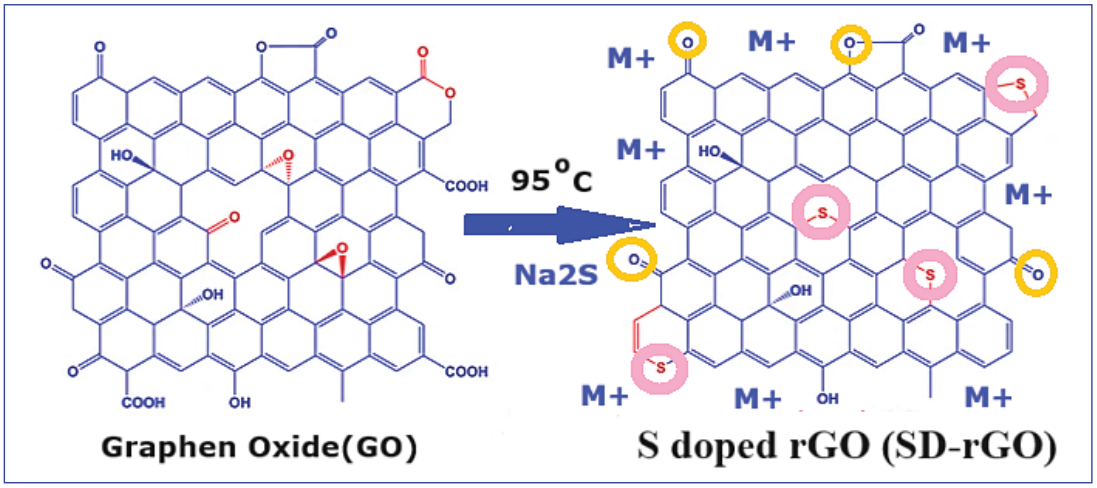

Fig. 1. Synthesis of sulfur-doped graphene oxide by Na_2S

2.4. Characterization

The field emission scanning electron microscopy (FE-SEM), XRD, and FTIR analysis characterized the S-doped graphene. FE-SEM images were obtained with a JEOL JSM-IT500 device. X-ray diffraction (XRD, Hitachi, Japan, EA8000A model, λ=1.5 Å) was used to analyze the crystalline nanostructures. Fourier Transform Infrared (FT-IR) spectra in the 400–4000 cm^{-1} range were achieved by the IR-Affinity-Shimadzu (Japan).

2.5. Description of the pilot

The designed drying sludge bed has an approximate volume of 0.6 cubic meters and sand layers with the size of sand from bottom to top (8 cm with 60 mm grain size, 6 cm with 18 to 25-grain size, 6 0 to 12 cm and 10 cm will be coarse grain sand). The material of the pilot body is stainless carbon with a thickness of 3 mm (Fig.2).

2.6. General procedure

To disinfect the sludge, it is enough to heat it twice at 60°C [21]. F-AAS and HG-AAS validated the heavy metal analysis with a polarography device. First, 10 mL of DW was mixed with 1.0 g of dried sludge with pure nitric acid (2% HNO_3), and then the solid phase was filtered with the Whatman filter (WF). The heavy metals (M: As, Cd, Cu, Pb, Hg, Mo, Ni, Co, Se, Zn) in 20 mL of the remaining solution of sludge and wastewater (µg L^{-1}) were extracted based on 30 mg of SD-rGO as solid-phase microextraction procedure (SPME) at pH 6.5 and then heavy metals back-extracted from adsorbent with eluent (1.0 mL, HNO3, 0.5 M) before being determined by the flame and hydride generation atomic absorption spectrometry (F-AAS; HG-AAS) after dilution up to 2.0 mL with DW. The results showed heavy metal concentrations were like the VT analysis after sample treatment. For the VT, 10 g of each drying sludge or sludge sample was prepared with 60 mL of 3.0 M of HNO_3 for 2 hours of stirring. Finally, the samples were vacuum filtered (200 nm, Watman filter) and put into Cole-Parmer Essentials Plus Class A (100 mL, Canada), which was kept at 0°C before determining heavy metals. An aliquot of 0.1 mL of each sample was diluted up to 200 mL with DW for the VT measurements. The dilution solution was put into the voltammetry cell before being degassed by Ar/N_2 for 25 minutes. Then, heavy metal ions (M: Cd, Cu, Pb, Ni, Co,

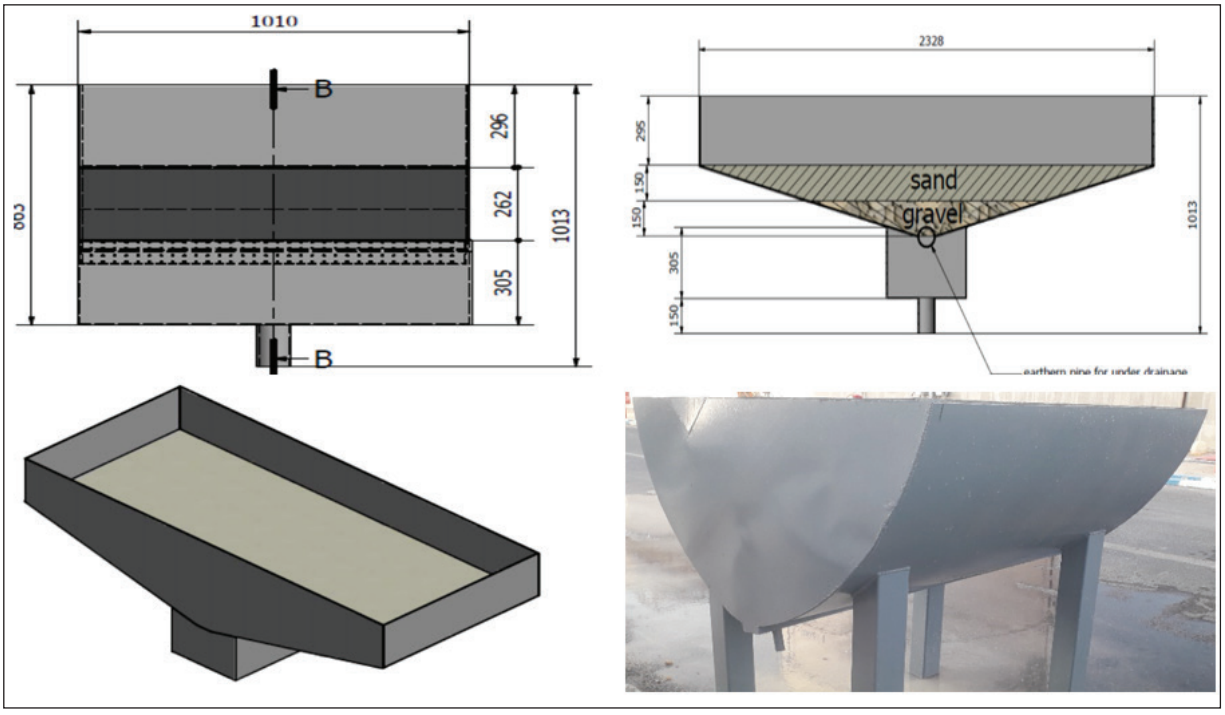

Fig.2. Image of the pilot design of the sludge dryer bed of the current project

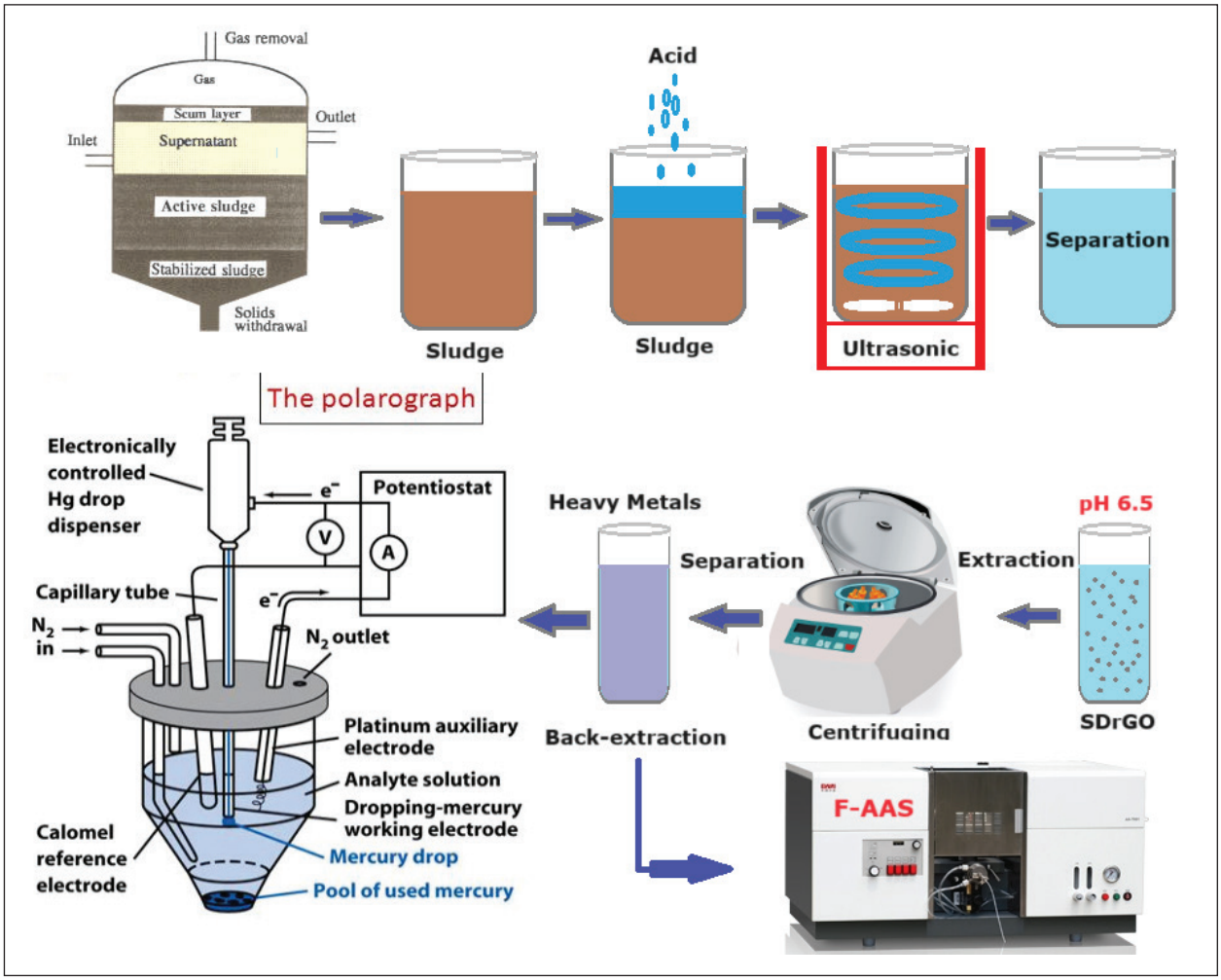

Fig.3. Procedure for extraction and determination of heavy metals by polarography and F-AAS

Zn) were deposited for 2.5 minutes at −1.2 V under stirring. (Fig.3) After 0.5 minutes, as equilibration time, the potential was scanned from −1.2 to 0.2 V by the anodic stripping voltammetry (ASV) mode (5 and 30 mV in square wave). Before peak integration, the VT software acquired baseline subtraction.

2.6.1.Measurement of sludge heavy metals with polarography

Voltammetry is an electrochemical method that, by measuring the amount of current in terms of potential changes in a three-electrode set, provides the possibility of qualitative and quantitative analysis of heavy metals in water and wastewater samples. This method is called polarography in special cases where the working electrode and a mercury drop electrode are used. This method allows qualitative and quantitative analysis of metals such as zinc, lead, tin, iron, nickel, cobalt, chromium, cadmium, etc. with high reproducibility. After equilibration time, the potential was scanned from −1.2 to 0.2 V by the anodic stripping voltammetry (ASV) mode.

2.6.2.Measurement of sludge heavy metals with AAS

All sample solutions were treated using SD-rGO adsorbent as an SPME procedure at pH 6.5. Then, after the back-extraction of heavy metals from SD-rGO adsorbent and dilution with DW, the concentrations of heavy metals were determined by F-AAS/HG-AAS.

3. Results and Discussion

3.1. FTIR spectra of SDGO

the FT-IR spectra of SD-rGO are shown in Figure 4. Based on the FT-IR spectrum, the peaks at 3458 cm^{-1} related to stretching vibrations of

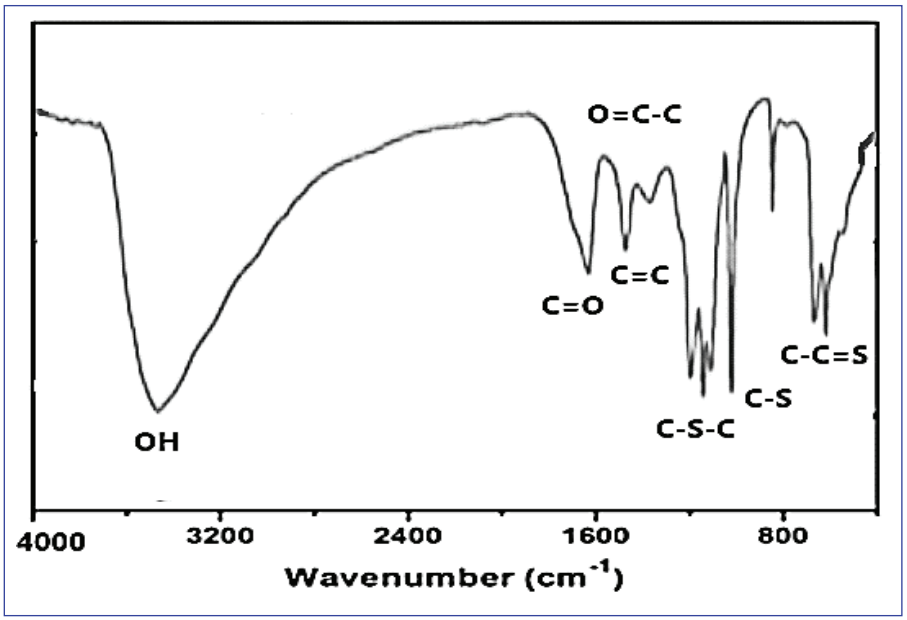

Fig. 4. FTIR spectra of SD-rGO adsorbent

-OH groups, 1628 cm^{-1} observed the carbonyl group(C=O), 1588 cm^{-1} peak showed carbon binding (C=C) and 1402 cm^{-1} are attributed to O=C–C bonding groups. Further, the peaks at 1201 cm^{-1}, 892 cm^{-1} and 575 cm^{-1} are related to the vibrations of C–S–C, C–S and C=S, respectively. The sulphur ions in Na_2S (negative charge) are absorbed with the carbonyl group (C=O) by the nucleophilic substitution mechanism.

3.2. XRS analysis

The XRD analysis of the pristine GO sheets and the SD-rGO sheets (2% sulphur doping) were obtained in Figure 5. Due to the XRD patterns, 30 mg of GO

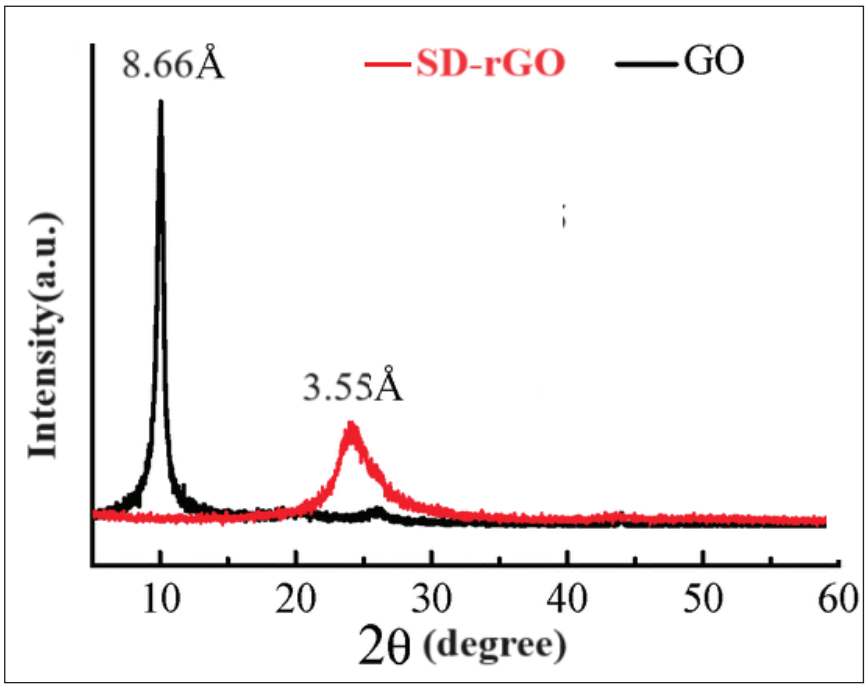

Fig.5. XRD Analysis of SD-rGO adsorbent

sheets have a sharp diffraction peak at 2θ =10.24° with an interlayer spacing of ~ 8.66 Å, related to the oxygen functional groups between graphene sheets. The SD-rGO adsorbent peaked at 2θ = 24.21° associated with an interlayer spacing of ~ 3.55 Å. Thus, the XRD results showed the structural restoration of the graphitic during the hydrothermal reaction.

3.3. SEM of SD-rGO adsorbent

The SEM of GO and SD-rGO is shown in Figure 6. The size of GO and SD-rGO was between 35-100 nm. In images, the SD-rGO is in the nanometer range, and functionalization of S- did not result in aggregation of rGO. The images showed that the functionalization sulphur on rGO does not change the general structure and morphology of rGO.

3.4. Sludge volume measurement

To determine the amount of sludge volume, the SVI criterion with the name of the sludge volume index will be used. In this method, a 100 mL cylinder of the sample is poured, and after 30 minutes, its sedimentation rate is measured. It is filtered by filter paper and dried in an oven at a temperature of 105°C, and the weight of the dry sludge is put into the following formula and calculated as the SVI [32]. (SVI: Sludge rate per 30-minute sedimentation rate)

3.5. Pilot control of sludge bed dryer

At this stage, first, the constructed sludge bed will be loaded with 200 litres of excess sludge from the sedimentation pond, whose volume index has already been measured, and the volume index of the output sludge will also be measured. Then, the pond is exposed to the ambient air for 120 hours to dry the sludge. The amount of heavy metals arsenic, cadmium, copper, lead, mercury, molybdenum, nickel, cobalt, and selenium is measured on it by a polarography and AAS device.

3.6. Optimization of pH, amount of adsorbent and sample volume for extraction in sludge

For efficient extraction of heavy metals, the amount of SD-rGO adsorbent between 5-50 mg has been examined in sludge samples by heavy metal concentration between 0.05-10 µg L^{-1} for Hg/As and 10-1000 µg L^{-1} for Cd/Cu/Pb/ Mo/ Ni/Se/Zn. The results showed that the maximum extraction of heavy metal ions in sludge samples

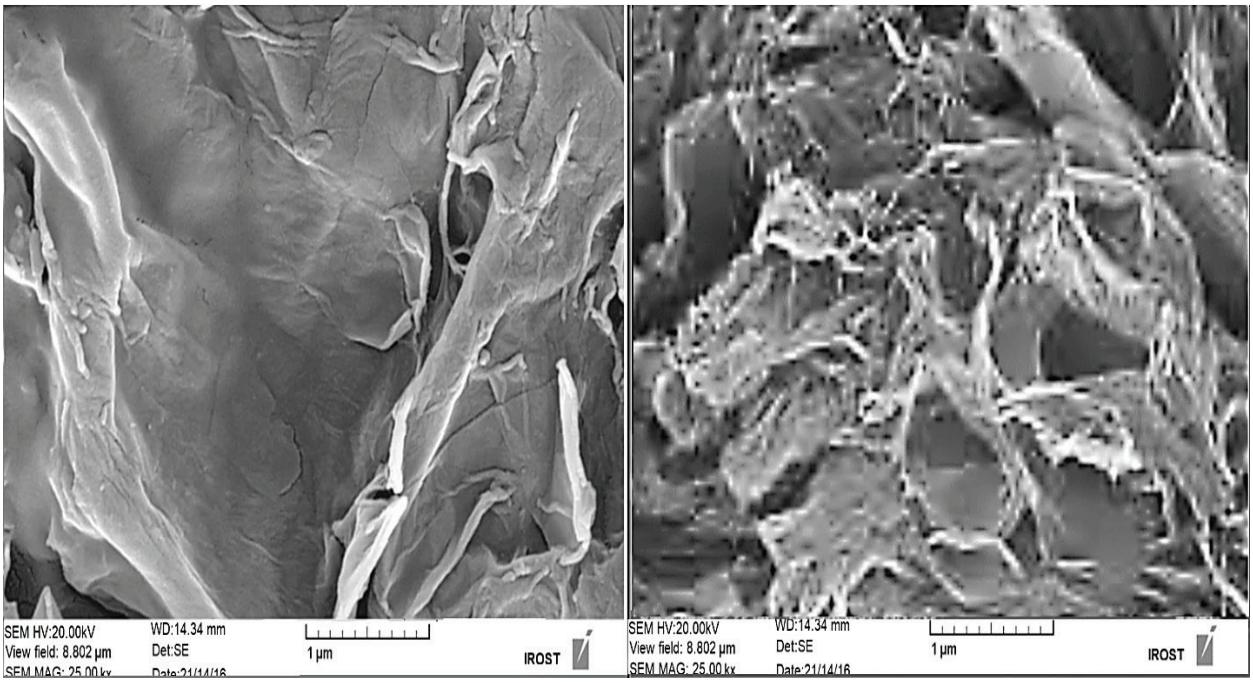

Fig.6. SEM of GO (Right) and SD-rGO (left)

was achieved at 30 mg of SD-rGO adsorbent at optimized conditions (Fig.7). The pH is the main factor for extracting heavy metals by SD-rGO adsorbent. Therefore, the various pH levels from 2 to 12 were studied in sludge samples through the buffer solutions. Due to the result, the best pH for Cd/Cu/Pb/Ni/Co/Zn concentration was obtained at 6.5 in sludge samples (Fig.8).

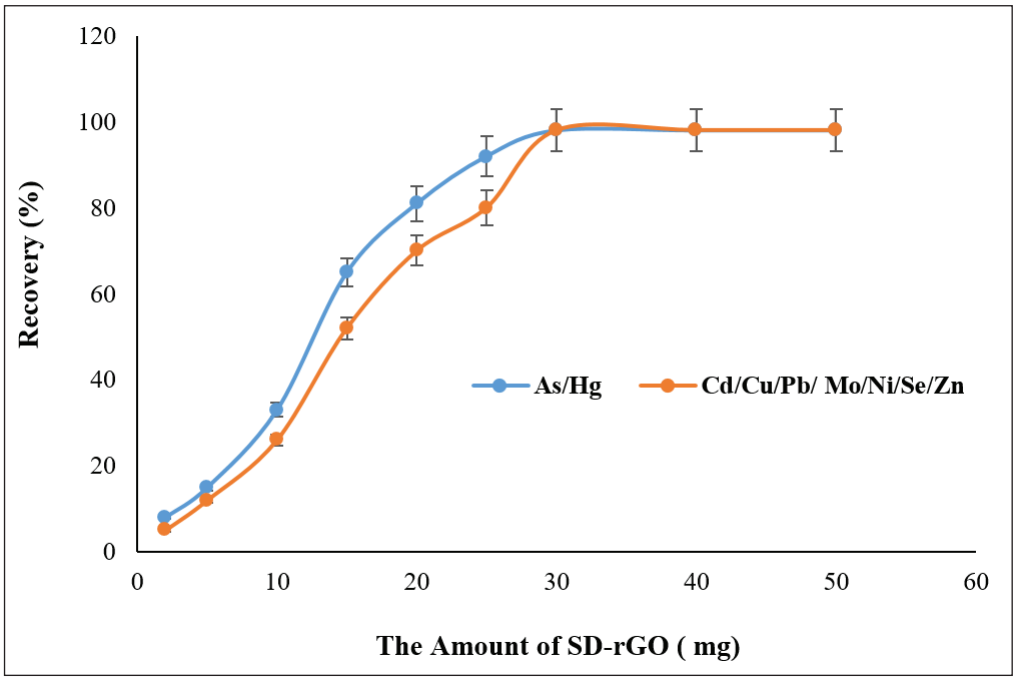

Fig.7. The effect of the amount of SD-rGO adsorbent on the extraction of heavy metals

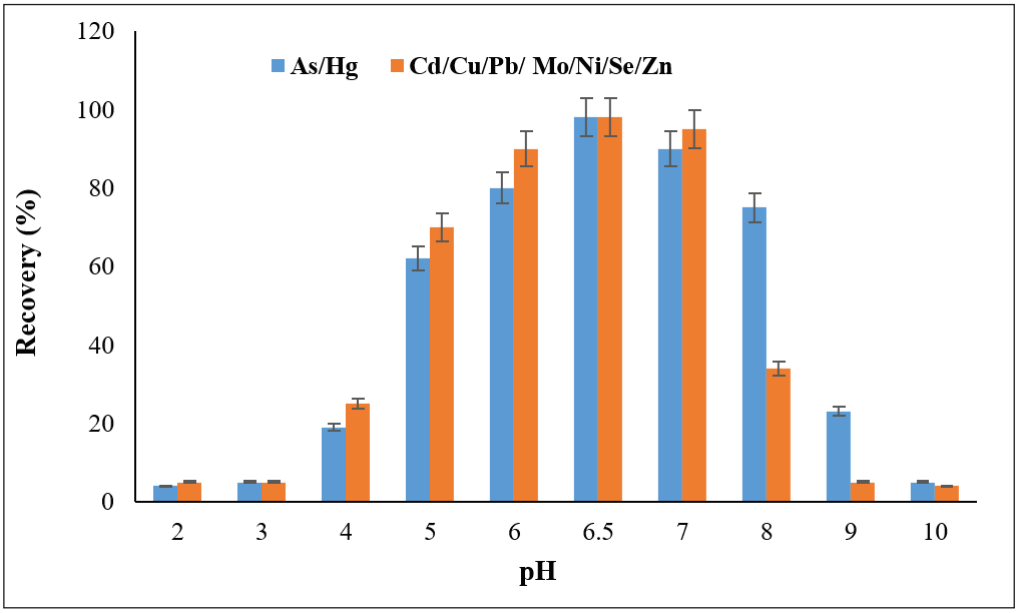

Fig. 8. The effect of pH on the extraction of heavy metals by the SD-rGO adsorbent

The extraction recoveries were decreased at less than a pH of 5 and more than 7. Also, the best volume for extraction was obtained at 20 mL. The various eluents such as HNO_3, HCl, and H_2SO_4 were used for back extraction of heavy metal ions from SD-rGO adsorbent. At low pH, the covalence bonding in S-Metal was broken, and metals were released in eluents. So, the procedure used the eluents (HNO3, HCl, and H2SO4) with different volumes and concentrations (0.2-0.8 mol L^{-1}, 0.2-2 mL). The results showed the HNO_3 (1 mL, 0.5 M) had maximum recovery.

3.7. Analysis in real samples

Table 1 shows the amount of SVI of the input and output of the sludge dryer. According to this table, the efficiency of removing SVI from the bed input has been 96% [33,34]. Table 2 and Figure 9 relate to the analysis of heavy metals in the output bed sludge by the polarography (Zn, Cd, Pb, Ni, Co,

Table 1. SVI of inlet and outlet wastewater sluge dryer

SVI	type
1900	sewage inlet bed
76	sewage outlet bed

Table .2 Concentration of heavy metals in dried sludge by polarography and F-AAS (mg kg^{-1})

Heavy Metals	Polarography	F-AAS	HG-AAS
As	-----	-----	0.048
Cd	0.041	0.039	-----
Cu	36.33	35.72	-----
Pb	0.096	0.101	-----
Hg	-----	-----	0.801
Mo	-----	-----	0.053
Ni	6.27	6.39	-----
Se	----	0.028	-----
Zn	8.69	8.92	-----
Co	5.23	5.18	-----

Table 3b. Standard concentration of pathogens in biological solids [35].

Concentration (MPN/100 mL)	Types of pathogens
191	Fecal coliforms
400	Total coliforms

MPN: Fecal coliform of organisms per 100 mL of sample water.
Maximum Acceptable Concentration for Drinking Water = no detected coliforms in 100 mL water.

Table 3a. The amount of digestive and fecal coliform in dried sludge

Concentration (MPN/100 mL)	Types of pathogens
191	Fecal coliforms
383	Total coliforms

MPN: Fecal coliform of organisms per 100 mL of sample water.
Maximum Acceptable Concentration for Drinking Water = no detected coliforms in 100 mL water.

Cu) and F-AAS. Also, the amount of digestive and fecal coliform in dried sludge and the standard concentration of pathogens in biological solids [35] are shown in Tables 3a and b. The standard concentration and loading rate of biological solids for use on land as sludge environmental standards are shown in Table 4 [35]. According to the results of Table 1, the dry sludge bed made in this research has a sludge removal efficiency of %96. The comparison of Tables 2 and 4 shows that the amount of heavy metals in the resulting sludge is by the environmental standards for use on the ground, and in this sense, there is no threat to the environment. On the other hand, comparing the results of microbiological analyses (Table 3a and 3b) with microbiological standards confirms the microbial standard of sludge. Therefore, the surplus sludge from this system can be used as compost in the green space with current conditions and disinfection at 60 degrees Celsius.

Table 4. Standard concentration and loading rate of biological solids for use on land [35].

Heavy metals	Max. Concentration (mg kg^{-1})	Concentration (mg kg^{-1})	Annual loading rate (mg kg^{-1})	Cumulative loading rate (mg kg^{-1})
As	75	41	2	41
Cd	85	39	1.9	39
Cu	4300	1500	75	1500
Pb	840	300	15	300
Hg	57	17	0.85	17
Mo	75	-	-	-
Ni/Co	420	420	21	420
Se	100	36	5	36
Zn	7500	2800	2	41

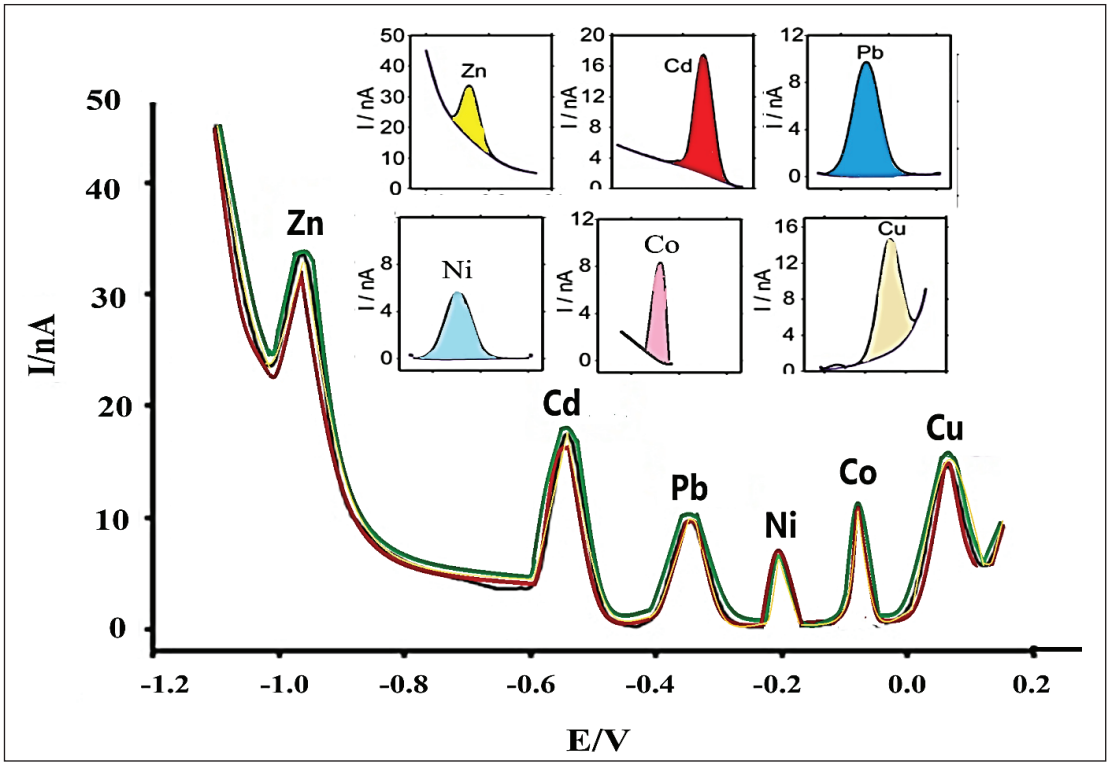

Fig. 9. Determination of heavy metals by the polarography (ASV mode)

4. Conclusion

Managing and controlling excess sewage sludge will be an important approach to preserving the environment and the health of living organisms in applications such as the cement industry and agriculture. Therefore, its purification is done by the methods of concentration, digestion, and dehydration, and its monitoring will prevent the entry of dangerous chemicals, such as heavy metals, into the environment. Therefore, in this research, a metal drying sludge package with an approximate capacity of 0.7 cubic meters with a bed of sand (8 cm with 60 mm grain size, 6 cm with 18 to 25-grain size, 6.0 to 12 cm and 10 cm will be coarse grain sand) was designed and built, which could reach 96% Physically remove excess sewage sludge. Considering the importance of the amount of heavy metals in the sludge, the concentration of these metals in the sludge obtained from the dryer sludge package was measured by polarography (ASV; ranges from 0.041 to 36.33 mg kg^{-1}) and atomic absorption methods (F-AAS, HG-AAS; ranges from 0.028 to 35.72 mg kg^{-1}). The results showed that the concentration of heavy metals in the resulting sludge is equal to standards and indicates the high-efficiency removal by packages (n=10, AAS: RSD<3% and CV: RSD<7%). Among the advantages of this package, we can mention the economical and changeable adsorbent bed so that in future research, we can use the method of sludge pretreatment with nanoabsorbents and change the bed of the dry sludge package to a large extent. So, the different amounts of heavy metals in the sludge are removed based on the changeable adsorbent bed. The package absorbed and removed the water coming out of the bed. As a result, this substrate can be widely used in the sewage industry due to its small volume and high sludge removal efficiency.

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