TRENDS IN SCIENCES 2023; 20(5): 5447 RESEARCH ARTICLE
https://doi.org/10.48048/tis.2023.5447

# Comparison of Modifiers for Coal Gangue Biochar Modification to Improve the Absorption of Heavy Metals from Aqueous Solution

**Hikmatullah Ahmadi[1], Yun Duan[1,*], Habibullah Sharifi[2], Sayed Hafiz Sadat[3], Mohammad Dawood Dawood[4], Shakeel Hussain[5] and Sayed Sanaullah Habibi[6]**

*[1]College of Environmental Science and Engineering, Taiyuan University of Technology, Shanxi 030024, China*
*[2]School of Civil Engineering, Central South University, Hunan 410017, China*
*[3]College of Civil Engineering, Taiyuan University of Technology, Shanxi 030024, China*
*[4]College of Electrical and Power Engineering, Taiyuan University of Technology, Shanxi 030024, China*
*[5]College of Mining Engineering, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China*
*[6]Postgraduate Student, Department of Agricultural Economics, Chaudhary Charan Singh Haryana Agricultural University, Haryana 125004, India*

**([*]Corresponding author's e-mail: duanyun@tyut.edu.cn)**

*Received: 31 July 2022, Revised: 4 September 2022, Accepted: 11 September 2022, Published: 8 March 2023*

## Abstract

In this paper, gangue Coal biochar GCC was developed to absorb heavy metals from an aqueous solution. There is currently insufficient information on the identification of the best biochar modifiers for the purpose of removing heavy metals as well as changes in physicochemical and morphological compositions after modification. For this purpose, after physical treatment GCC ware modified with 5 different offending chemical methods ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$). Physical and chemical changes in Both modified and unmodified GCC properties were investigated by using (XRF), (FT-IR), (XRD), (SEM-EDX), and (BET) assortment. Adsorption tests of 3 heavy metals (Cu, Pb, and Cd) ions under different conditions, ion concentration, pH, Adsorbent dosage, and contact time were investigated in batch experiments. Improved post-modification GCC properties, especially ($GCC_{alkaline}$) and ($GCC_{MnOx}$) Significant changes in its surface area as well as functional groups (hydroxyl group, and Manganese oxide group). To will know adsorption capacity of every modified GCC, experimental data were placed in Langmuir and Freundlich's isotherms models. The GCC process follows pseudo-second-order and pseudo-first-order kinetic curves with linear regression. GCC modified with Manganese oxide shows it has the best adsorbent for adsorption of Pb and GCC modified with alkaline is the best adsorbent for adsorption of Cd and Cu metals. For adsorption of mixed metals solution (Pb, Cd, and Cu) $GCC_{MnOx}$ was more suitable than other GCC and modified GCCs biochars. The results show that GCC modified with an acidic component is the worst attraction for removing heavy metals from an aqueous solution.

**Keywords:** Gangue coal modification, Pb, Cd, and Cu metals removal competitive, Physicochemical adsorbent properties investigation and competition

## Introduction

In today's society, with the rapid development of the economy, the environment on which human being's lives is also suffering from more and more serious pollution, resulting in a series of environmental problems such as water pollution, air pollution, and soil pollution [1]. In recent years, the rapid development of industry and agriculture and the acceleration of urbanization have made most areas of world have different levels of pollution problems. A large amount of industrial wastewater, domestic sewage and solid waste will cause serious pollution after being discharged into soil and water bodies. Among the many pollutants, heavy metal pollution has attracted widespread attention due to its wide range of pollution, difficult governance and serious consequences [2] Heavy metals Entered water systems (lakes, rivers, streams, and groundwater) Due to industrial activities such as battery manufacturing, electronics industry, metallurgy industry, electronic plating, and mining [3]. And these heavy metals accumulate in humans, animals, and vegetation that enters the body through the skin, membranes, swallowing, and inhalation and is very harmful [4-6]. That is why the removal of heavy metals from the water system is a very necessary task [7].

Due to the removal of heavy metals from the water system, various technologies have been created, including ion conversion, filtering, electrolysis, membrane, and Adsorption [8,9]. Adsorption is wildly using in the world because of its ease system, the ability to change the system and it is cheaper for removal of metals from the water system [10].

Among the attractions, biochar is one of the most widely used materials due to its amazing capabilities such as surface radiance, stable structure, cation exchangeability, low cost, and high carbon to absorb organic and inorganic matter [11,12]. Biochar has a lot of carbon and is obtained by heating and limiting oxygen and has a negative charge its suitable for heavy metals which has a positive charge to absorb [13]. Biochar uptake capacity depends on morphology such as large surface area, pores, and biochar function groups [14]. Much research has been done on the carbonization of biochar by heat [15].

Biochar gravity capacity has been improved using various modification methods in recent years [13]. For example, the Mg-modified biochar for Pb removal is noteworthy, which increases the ability of absorbent gravity several times [16]. At present, there is not much research on which modification is good for improvement of biochar, and most research is scattered. Comparisons between modifiers are very small [16]. Different environmental conditions are also a challenge for not knowing the modifiers better [11].

Comparing the modifier and knowing the best modifier for biochar modification and changes in biochar morphology is essential for the adsorption of heavy metals It is especially in different environmental conditions. For this reason, 5 modifiers(acidic), (alkaline), (oxidic), (MnOx), and (FeOx) were studied to modify gangue Coal biochar to remove metals heavy (Cu, Pb, and Cd) from an aqueous environment and changes in GCC morphology and microstructures.

## Materials and methods

### Materials

We got gangue coal from Taiyuan/Shanxi/China. The main components of $GC_{row}$ (57.7 % $SiO_2$, 24.2 % $Al_2O_3$, 1.58 % $TiO_2$, 6.4 % $Fe_2O_3$, 1.7 % MgO and CaO, S, K2O, others, LOI, 1.59, 0.95, 3.23, 0.38 and 2.28 % (by using XRF). After receiving $GC_{row}$, first it was washed several times with purified water, then it was dried at room temperature. by using friction grinder to powders and passed through a 200 mesh sieve. lead nitrate ($Pb(NO_3)_2$, > 99.0 %), ($CuCl_2$. 2.5 $H_2O$, > 99 %), ($CdCl_2$. $H_2O$, 98 %). hydrochloric acid (HCL), hydrogen peroxide ($H_2O_2$, 30 %), Potassium permanganate ($KMnO_4$, > 99 %), $FeCl_3$ and NaOH ware purchased from TYUT.

### Preparation of modify GCC

For the preparation of biochar, the GCC was first under pyrolysis conditions in the range of 800 °C for 2 h to reduce the carbon content. Then 5 different methods of chemical activation were used to modify GCC. For GCC (acidic, alkaline, and oxidic) activation shaking GCC in 3 M of HCl, 3 M of NaOH, and 10 % of H2O2 in a solid/liquid proportion of 40 g/L while stirring at 180 rpm over 1 day/night. To modify GCC by MnOx and FeOx methods using 3 M of $KMnO_4$ and 3 M of $FeCl_3$ in a solid/liquid proportion of 40 g/L while stirring at 180 rpm over 1 day/night. Modified $GCC_{KMnO4/FeCl3}$ stirring with 100 mL of HCl/NaOH for 1 h at 250 rpm then washed with distilled water several time until pH was Natural. We then dried the washed samples over a period of 24 h in an oven set at 60 °C before using them in the experiments.

### Physico-chemical characterization

To analyze the function group of CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$) samples by using Fourier transform infrared spectrophotometer (FTIR, PerlnElmer, L1600400 spectrum Two FT-IR, UK) from 4,000 to 400 $cm^{-1}$ through using KBr technique. We analyzed the chemical compositions and crystal structures of modified and unmodified CCG samples by using an X-ray fluorescence (XRF) spectrometer, and X-ray diffraction spectroscopy (XRD, Malvern panalytical, 7602EA, Netherland). We used a scanning electron microscope (SEM, EDX, TESCAN MIRA LMS-Oxford Xplore 30) to study morphology, chemical composition, and microstructure of the CCG and the modified CCG. To determine the Pores and specific surface area of the (GCCacidic), (GCCalkaline), (GCCoxidic), (GCCMnOx), (GCCFeOx), and GCC by using the Brunauer-Emmett-Teller (BET) method. Atomic absorption spectrometry AAS (PerkinElmer Analyst 400) was used to measure metals concentrations.

**Adsorption test**

The uptake of heavy metals (Cu, Pb, and Cd) by CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$) from an aqueous solution was Comparison investigated in a batch experiment. in a 100 mL flask with a 50 mL of condiment. by using the following operating parameters: pH (2 - 8), biosorbent amount (1 - 10 g/L), metals concentration initial (100 - 1,000 mg/L), adsorption period (5 - 100 min), at temperature of 30 °C at 180 rpm. The effect of pH on adsorption of (Cu, Pb, and Cd) metals was investigated using 10 g/L biosorbent and initial concentration of 100 mg/L in a 50 mL suspension volume shacked for 24 h. At optimum pH, the effect of adsorbent amount on (Cu, Pb, and Cd) metals adsorption was examined by adsorbent increasing from 1 to 10 g/L, at 30 °C, the fancy volume of 50 mL 1,000 mg/L of metals concentration was shaken at 180 rpm for duration of 24 h. effect of time was investigated from 5 to 100 min in 1,000 mg/L adsorbate with 4 g/L of adsorbent stared at 180 rpm at optimum pH. effect of metals concentration incorrect from 100 to 1,000 mg/L using 4 g/L adsorbent for 45 min at 180 rpm optimum pH. for well known the equilibrium time of CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$) to adsorb (Cu, Pb, and Cd) metals kinetic study was performed, by adding 100 mL of (Cu, Pb, and Cd) metals single metal solution with the metal concentrations of 1,000 mg/L and 4 g of the adsorbent with different period times from 5 to 100 min, in temperature of 30 °C at 180 rpm. Adsorption isotherms are tested through equilibrium experiments of (Cu, Pb, and Cd) metals single metal adsorption onto the CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$) by stirring 4 g/L of adsorbent in 50 mL solution of (Cu, Pb, and Cd) metals with different initial concentrations (100 - 1,000 mg/L) At optimal pH and 180 rpm for 45 min. all samples were centrifuged for 15 min at 4,000 rpm, then solution was filtered through 42 µm membrane filter paper and the amount of metals in the filtered solution was read by an atomic absorption spectrometer. Three replications were considered for each treatment. Eqs. (1) and (2) were used to calculate the capacity of adsorption (qe) and R% Removal efficiency of the GCCs at equilibrium:

$$R\% = \frac{C_0 - C_e}{C_0} * 100 \tag{1}$$

$$q_e = \frac{C_0 - C_e}{m} * v \tag{2}$$

Co initial concentration of metals in solution mg/L, Ce concentration of metals in solution mg/L after adsorption. m is the adsorbent mass (g), and v is the volume of the solution (Liters). To study the metals adsorption isotherm, Langmuir models in Eq. (4) and Freundlich Eq. (3) were used with linear form of the equations:

$$Log\ q_e = Log\ K_f + \frac{1}{n}\ Log\ C_e \tag{3}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{C_e}\left(\frac{1}{k_1} q_m\right) \tag{4}$$

In these equations, Kf and n are the constants of the Freundlich equation, kl is the constant of the Langmuir equation in relation to the adsorption energy (L.mg) and qm the maximum adsorption (mg/g), of metals as a monolayer.

The kinetics of metals adsorption were evaluated by pseudo-first-order kinetic and pseudo-second-order kinetic equations, Eqs. (5) and (6). These equations are mathematically expressed as follows:

$$L_n\left(q_f - q_t\right) = L_n\, q_f - K_1 t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2} q_f^2 + \frac{t}{q_f} \tag{6}$$

$q_f$ and $q_t$ are amount of metal adsorb by Adsorbent (mg/g) at equilibrium and related time (t), k1 represents pseudo-first-order rate constant (L/min), and k2 represents pseudo-second-order rate constant (min-L.mg/g-L).

## Results and discussion

### Effect adsorption parameter process

The Effect of the contact time on adsorption of (Cu, Pb, and Cd) metals by CCG and (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$) in **Figure 1** at shows that in 45 min all the adsorbents were almost reached equilibrium, and the absorption was rapid in the first 15 min and almost 50 % of the adsorption was done due to the active groups and purse of GCC given this ability to adsorbents. After about 45 min, almost all the attraction of the adsorption process was silenced. The highest adsorption was done after 45 min by GCC$_{MnOx}$ for adsorption of Pb 162.5 mg/g and GCC$_{alkaline}$ adsorb Cd and Cu 143.5 mg/g and 139.5 mg/L, the lowest adsorption was by GCC$_{acidic}$ (Pb 115.5 mg/g, Cd 112.5 mg/g and Cu 101.25 mg/g) and GCC (Pb 118.25 mg/g, Cd 97.25 mg/g and Cu 92 mg/g).

Effect of the Adsorbent Dosage was done by increasing the adsorbent dose from 1 - 10 g The effect of adsorbent dosage on the elimination of (Cu, Pb, and Cd) metals is shown in **Figure 2** Experiments demonstrated that as the adsorbent dosage is increased, the percentage of metal ions removed increases as well. The increased number of functional groups/convenient adsorption sites for metal ions was the cause of this rise. It also shows with increase adsorbent dosage adsorption capacity was decrease. It may be due to the overlap and accumulation of adsorbents next to each other and thus reduce the total amount of adsorbent surface and adsorption attraction, which will ultimately reduce the efficiency of heavy metals adsorption [17]. When GCC$_{MnOx}$ dosage reached to 10 g/L the adsorption capacity for pb removal decreased about 99 mg/g it shows 99.1 % removal but in 1 g/L GCCMnOx adsorption capacity for pb was 340 mg/g with 34 % removal. Also for GCC$_{alkaline}$ dosage reached to 10 g/L Cu and Cd metals 96.6 and 92.1 % removal. the lover adsorption removal after 10 g/L GCC Pb, Cd and Cu ware 82.3, 76.9 and 66.9 present for GCC$_{acidic}$ with 86.3, 84.1 and 76.9 % respectfully.

Investigations Effect of the initial concentration of (Cu, Pb, and Cd) metals into CCG and (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$) adsorption. is shown in **Figure 3** With increasing the concentration of metals from 100 to 1,000 mg/L, the CCG and (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$) adsorption capacity also increased at a specific point, and when it reaches to the equilibrium After saturation, the adsorption almost became silent, and pores are filled and saturated active groups. The presence of these active groups can be a sign of the concentration gradient, which Plays an important role in the adsorption of metals. Additionally, by increasing the concentration gradient, the force of propulsion between liquid and solid can also be increased, allowing the mass transfer resistance between them to be overcome and the absorption rate to be increased. When GCC$_{MnOx}$ initial concentration was 1,000 the adsorption capacity for pb increased to about 162.5 mg/L and the lowest with an initial concentration of 100 mg/L by adsorption of 22.75 mg/g. Also for GCC$_{alkaline}$ initial concentration of 1,000 Cu and Cd metals, the adsorption capacity is below 143 and 139 mg/g with 100 mg/L the lowest 19.5 and 18.25 mg/L. the lover adsorption removal was GCC and GCC$_{acidic}$ with 36 and 45 mg/g respectively.

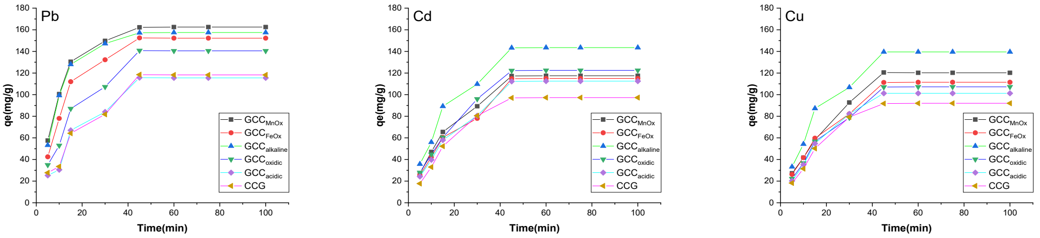


**Figure 1** Effect of contact time on the adsorption of (Cu, Cd and Pb) metals into CCG and (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$).

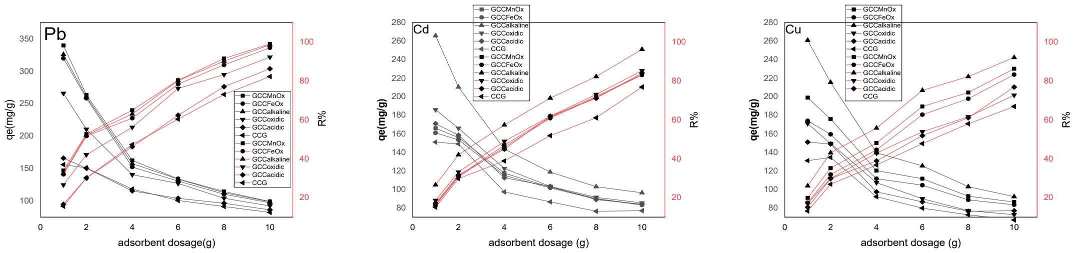


**Figure 2** Effect of adsorbent dosage on the adsorption of (Cu, Cd and Pb) metals into CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$).

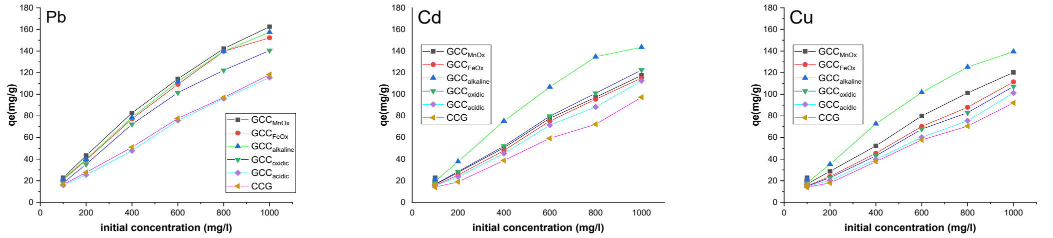


**Figure 3** Effect of initial concentration of (Cu, Cd and Pb) metals adsorption into CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$).

The effect pH on adsorption of Cu, Cd and Pb metals by CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$) shown in **Figure 4** With increasing pH from 2 to 6, the efficiency of heavy metals adsorption also increased by all modified and unmodified GCC. The highest removal of (Cu, Pb, and Cd) metals from the solution was observed at pH of 5 and 6 for all 6 adsorbents. ($GCC_{alkaline}$) and ($GCC_{MnOx}$) at 5 pH < 99 % removals of (Cu, Pb, and Cd) metals, for ($GCC_{acidic}$), ($GCC_{oxidic}$) and GCC at 6 pH < 99 % removals of (Cu, Pb, and Cd) metals, for ($GCC_{FeOx}$) at 6 pH < 99 % removals of (Cu, Cd) metals and at 5 pH < 99 % removals of (Pb) metal. By increasing pH from 6, the adsorption efficiency of heavy metals by all adsorbents decreased. One of the most important factors affecting the adsorption process is pH environments because, on the 1 hand, hydrogen ions are strongly affected. Metal ions compete for adsorption sites and, on the other hand, determine the chemical ion shape of the metal and the degree of ionization of the adsorbent during the reaction [18,19]. At low pH a lot of H+ and H3O+ Present in the solution at possible Cation present in heavy metals Compete for attraction of adsorbent active sites [20]. It is probably the result of the formation of heavy metals hydroxyl complexes in solution (M(OH)+) and insoluble (M(OH)2) and its competition with active adsorbent sites, so the retention of heavy metals ions on adsorbents sites is reduced [21]. As result the best pH was between 5 and 6 for those heavy metals adsorption by GCCs.

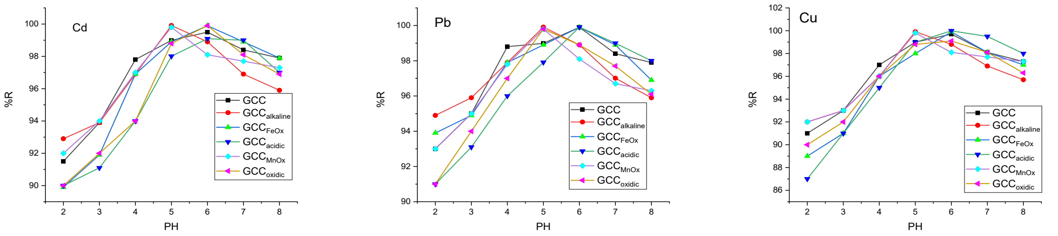


**Figure 4** Effect of pH on the adsorption of (Cu, Cd and Pb ions) into CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$).

### Analysis of adsorbent characterizations

According XRD patterns in **Figure 5** quartz (SiO$_2$) and illite (KAl2Si3O10(OH)2) in the CCG and (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$) are main crystallized minerals. XRD diffraction data also indicates a decrease in the severity of the GCC adsorbent when compared to the modified samples, increasing amorphous properties and decreasing Crystallite size was found by adding alginate. The main Impure elements of the GCC and the modified adsorbent components is quartz, which is explicit in the XRD analysis where the main diffraction peak at 2$\theta$ = 20.09, 26.66 and 42.2 which related to (010), (101) and (020) planes. Furthermore, quartz and illite exhibit identical diffraction planes in both CCG as well as the modified adsorbent composite.

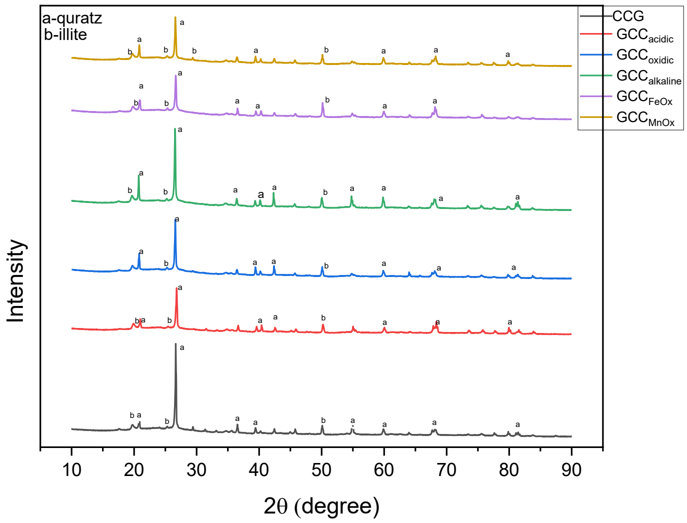


**Figure 5** XRD spectra of CCG and (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$).

As shown in the **Table 1** gangue coal"s changes in physical properties before and after heating, as well as after chemical modification. Physicochemical properties determine the quality of biochar. After 2 h of heating 8,000 °C, GC$_{ROW}$ surface area surpasses 28 m$^2$/g. It had been 23 m$^2$/g before heating. After modification, the surface area of modified GCCs increases to between 29 and 47 m$^2$/g. the surface area of GCC$_{acidic}$ 37 m$^2$/g, GCC$_{alkaline}$ 43 m$^2$/g, GCC$_{oxidic}$ 35 m$^2$/g, GCC$_{MnOx}$ 47 m$^2$/g, and GCC$_{FeOx}$ is 29 m$^2$/g. as the result GCC$_{MnOx}$ and GCC$_{alkaline}$ has larger area after modifications its more suitable for adsorption. There is also an improvement in the pour size of coal gangue biochar after modifications. The average Pore size of GCC$_{acidic}$ 5.9 nm, GCC$_{alkaline}$ 7 nm, GCC$_{oxidic}$ 4.9 nm, GCC$_{MnOx}$ 6.7 nm, and GCC$_{FeOx}$ is 5.3 nm while before modification GCC 4.1 nm and GC$_{ROW}$ 3.4 nm. BET analysis shows an increase in the surface area of adsorbent Pores, which is important for the adsorption of heavy metals (Cu, Pb, and Cd) metals.

**Table 1** BET analysis of the before and after heating as well after chemical modification.

| **Modification** | **Surface area** | **Total pore volume** | **Average pore diameter** |
|---|---|---|---|
| **method** | **(m$^2$/g)** | **(cm$^3$/g)** | **(nm)** |
| GCC$_{MnOx}$ | 47 | 0.041 | 6.7 |
| GCC$_{FeOx}$ | 29 | 0.033 | 5.3 |
| GCC$_{alkaline}$ | 43 | 0.044 | 7 |
| GCC$_{oxidic}$ | 35 | 0.037 | 4.9 |
| GCC$_{acidic}$ | 37 | 0.042 | 5.9 |
| GCC | 28 | 0.031 | 4.1 |
| GC$_{ROW}$ | 23 | 0.030 | 3.4 |

The **Figure 6** represent functional groups on the surfaces of CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$) by FT-IR analysis, as analyzed by XRD and XRF the present of the main components Si-O-Si, Si-O, Mn-O and Fe-O are at frequencies (1,020 - 1,070 cm, and 620 - 680 cm). The O-H groups are seen at ranges 3,350 - 3,450, the C-H at ranges 2,850 - 2,950, the C = O and C-N at ranges 1,900 - 1,600 cm but it Changed a bit on their violent Included, those groups present in all modified and unmodified GCC. Based on the FT-IR spectra of ($GCC_{alkaline}$ and $GCC_{MnOx}$) samples, the main peaks were slightly increased, as a XRD and EDX result suggested SiO elements is increased. It was found that all modifications led to an increase in oxygen groups such as HO, C = O, Manganese-oxide, and Iron-oxide in all modified GCC types, however with slightly changes their functional groups were formed due to the modification methods.

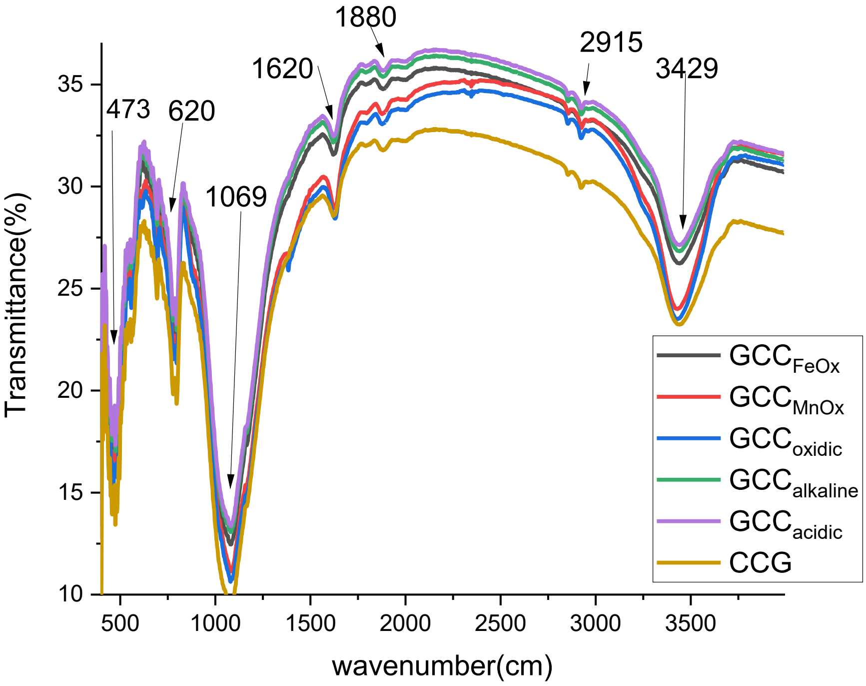
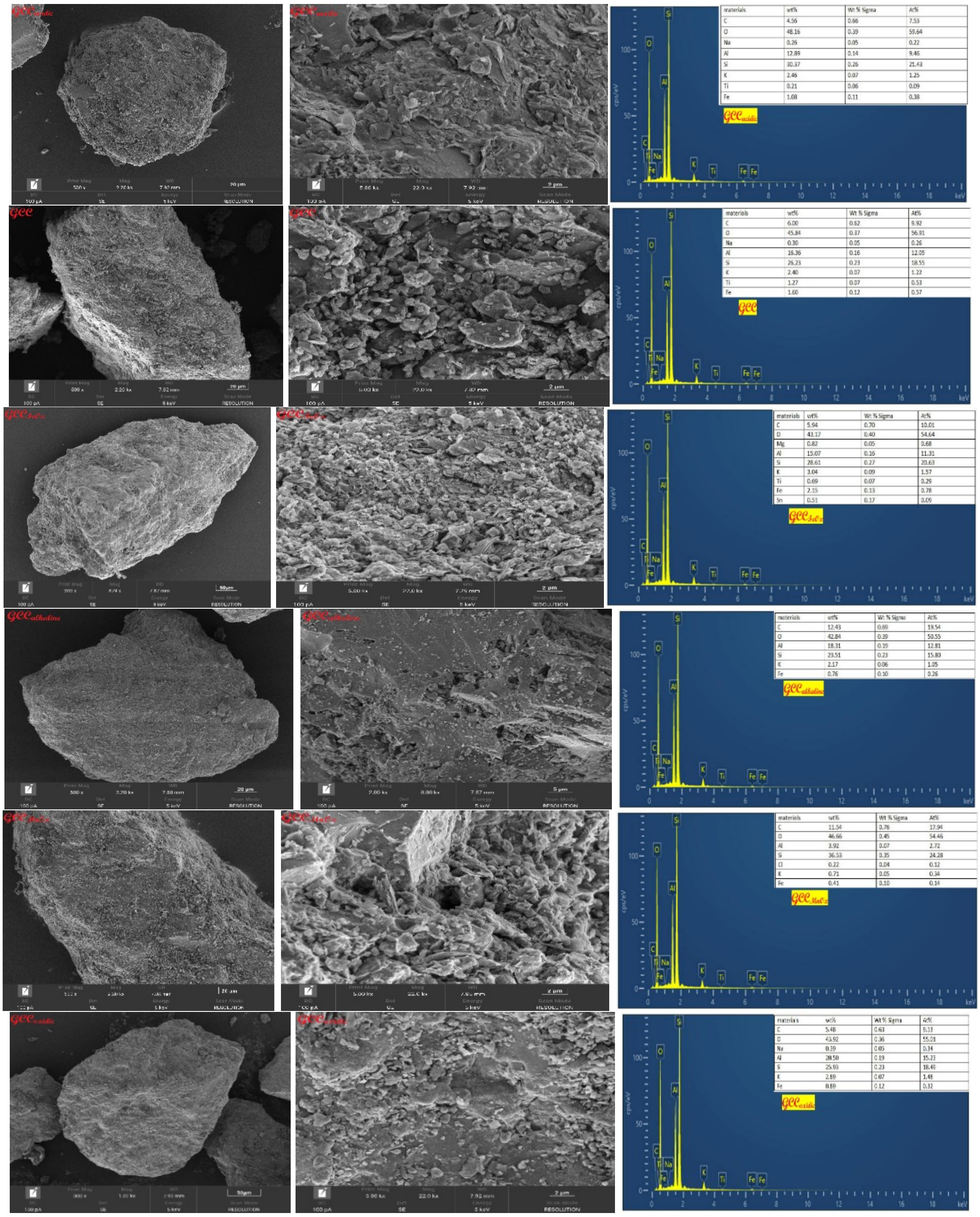


**Figure 6** FTIR spectra of CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$).

Using SEM and EDX to see Changes in the structures and morphology of gangue Coal before and after modification are evaluated in **Figure 7** Some morphological change of GCC structure after modification with 5 modifiers. The surface of the $GCC_{FeOx}$ and $GCC_{acidic}$ is much smoother than the Unmodified GCC. While on surface of $GCC_{MnOx}$ and $GCC_{alkaline}$ a rough and small partials can be seen, except with purse it seems more then $GCC_{acidic}$ and $GCC_{oxidic}$. The $GCC_{oxidic}$ is smoother than The $GCC_{MnOx}$ and $GCC_{FeOx}$, but holes appear smaller. As can be seen on the surface of the unmodified gangue Coal, the surface is not rough and are pores small due constant carbon, Silicon material also causes this irregularity, which was mentioned earlier. But after the gangue Coal has been modified, the surface has changed and it seems to have a smooth and regular surface.



| materials | wt% | Wt % Sigma | At% |
|---|---|---|---|
| C | 4.56 | 0.66 | 7.53 |
| O | 48.16 | 0.39 | 59.64 |
| Na | 0.26 | 0.05 | 0.22 |
| Al | 12.89 | 0.14 | 9.46 |
| Si | 30.37 | 0.26 | 21.43 |
| K | 2.46 | 0.07 | 1.25 |
| Ti | 0.21 | 0.06 | 0.09 |
| Fe | 1.08 | 0.11 | 0.38 |

| materials | wt% | Wt % Sigma | At% |
|---|---|---|---|
| C | 6.00 | 0.62 | 9.92 |
| O | 45.84 | 0.37 | 56.91 |
| Na | 0.30 | 0.05 | 0.26 |
| Al | 16.36 | 0.16 | 12.05 |
| Si | 26.23 | 0.23 | 18.55 |
| K | 2.40 | 0.07 | 1.22 |
| Ti | 1.27 | 0.07 | 0.53 |
| Fe | 1.60 | 0.12 | 0.57 |

| materials | wt% | Wt % Sigma | At% |
|---|---|---|---|
| C | 5.94 | 0.70 | 10.01 |
| O | 43.17 | 0.40 | 54.64 |
| Mg | 0.82 | 0.05 | 0.68 |
| Al | 15.07 | 0.16 | 11.31 |
| Si | 28.61 | 0.27 | 20.63 |
| K | 3.04 | 0.09 | 1.57 |
| Ti | 0.69 | 0.07 | 0.29 |
| Fe | 2.15 | 0.13 | 0.78 |
| Sn | 0.51 | 0.17 | 0.09 |

| materials | wt% | Wt % Sigma | At% |
|---|---|---|---|
| C | 12.43 | 0.69 | 19.54 |
| O | 42.84 | 0.39 | 50.55 |
| Al | 18.31 | 0.19 | 12.81 |
| Si | 23.51 | 0.23 | 15.80 |
| K | 2.17 | 0.06 | 1.05 |
| Fe | 0.76 | 0.10 | 0.26 |

| materials | wt% | Wt % Sigma | At% |
|---|---|---|---|
| C | 11.54 | 0.76 | 17.94 |
| O | 46.66 | 0.45 | 54.46 |
| Al | 3.92 | 0.07 | 2.72 |
| Si | 36.53 | 0.35 | 24.28 |
| Cl | 0.22 | 0.04 | 0.12 |
| K | 0.71 | 0.05 | 0.34 |
| Fe | 0.41 | 0.10 | 0.14 |

| materials | wt% | Wt % Sigma | At% |
|---|---|---|---|
| C | 5.48 | 0.63 | 9.13 |
| O | 43.92 | 0.36 | 55.01 |
| Na | 0.39 | 0.05 | 0.34 |
| Al | 20.50 | 0.19 | 15.23 |
| Si | 25.93 | 0.23 | 18.49 |
| K | 2.89 | 0.07 | 1.48 |
| Fe | 0.89 | 0.12 | 0.32 |

**Figure 7** SEM and EDX spectra of CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$).

### Adsorption isotherms

Examination of isotherms under Cu, Cd and Pb metals with deferent concentration was shown in **Figure 8** Isotherms provide useful information about attractions and mechanism of adsorption between the adsorbate and adsorbent. The presents parameters fitting in Langmuir and Freundlich models with linear regression. The adsorption conduct of CCG and (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$) for removal of Cu, Cd and Pb metals ware investigated by using Langmuir and Freundlich's isotherm models. Langmuir's model provided a better fit than Freundlich's. This suggests that the Cu, Cd and Pb metals adsorption on modified and unmodified GCC was largely conducted at the functional groups/binding sites of the adsorbent, and the Adsorption occurred as a monolayer chemisorption. On the other hand, the Freundlich's isotherm suggests that adsorption heterogeneous surface of the adsorbent. according **Table 2**. It shows Langmuir isotherm R2 value with linear regression for Pb metal into CCG and (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$) every adsorbent, value between (R2 < 92 - 98). For Cd metal R2 value into (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$) adsorbent value between (R2 < 91 - 99) and CCG (R2 < 83). For Cu metal R2 value into (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$), adsorbent value between (R2 < 90 - 99) for CCG and (GCC$_{acidic}$) R2 78.7 and 84.8. Langmuir isotherm R2 value with linear regression for Cu, Cd and Pb metal into CCG (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$) every adsorbent, value between (R2 < 92 - 98). the maximum adsorption capacity of Cu, Cd and Pb metals into CCG (73.4, 80.9 and 126.7 mg/g) and (GCC$_{acidic}$), (83.1, 111.7 and 117.2 mg/g), (GCC$_{alkaline}$), (331.8, 270.2 and 156.9 mg/g), (GCC$_{oxidic}$), (100.3, 132.4 and 370.3 mg/g), (GCC$_{MnOx}$), (126.5, 125.4 and 150.6 mg/g), (GCC$_{FeOx}$), (111.8, 121.9 and 182.8 mg/g) ware founded respectively.

**Table 2** Isotherms parameters for the removal of Cu, Cd and Pb metals by CCG and (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$).

| Adsorbents | Isotherms | Metals | Qmax (mg/g) | Kl | Rl | R2 |
|---|---|---|---|---|---|---|
| **GCC$_{MnOx}$** | Freundlich | Pb | 150.6024096 | 0.019171 | 0.510584 | 0.97857 |
| **GCC$_{FeOx}$** | | | 182.8153565 | 0.007879 | 0.717383 | 0.98181 |
| **GCC$_{alkaline}$** | | | 156.9858713 | 0.011915 | 0.626669 | 0.96331 |
| **GCC$_{oxidic}$** | | | 370.3703704 | 0.00183 | 0.91617 | 0.99513 |
| **GCC$_{acidic}$** | | | 117.2332943 | 0.004144 | 0.828357 | 0.92256 |
| **CCG** | | | 126.7427123 | 0.004202 | 0.826376 | 0.95351 |
| **GCC$_{MnOx}$** | Freundlich | Cd | 125.4705144 | 0.004251 | 0.82472 | 0.95281 |
| **GCC$_{FeOx}$** | | | 121.9512195 | 0.003789 | 0.84072 | 0.92904 |
| **GCC$_{alkaline}$** | | | 270.2702703 | 0.003512 | 0.850644 | 0.99686 |
| **GCC$_{oxidic}$** | | | 132.4503311 | 0.004194 | 0.826645 | 0.95625 |
| **GCC$_{acidic}$** | | | 111.7318436 | 0.003812 | 0.839922 | 0.91531 |
| **CCG** | | | 80.97165992 | 0.00436 | 0.821019 | 0.83277 |
| **GCC$_{MnOx}$** | Freundlich | Cu | 126.5822785 | 0.004628 | 0.812071 | 0.95247 |
| **GCC$_{FeOx}$** | | | 111.8568233 | 0.003815 | 0.839798 | 0.92337 |
| **GCC$_{alkaline}$** | | | 331.1258278 | 0.002152 | 0.902861 | 0.99398 |
| **GCC$_{oxidic}$** | | | 100.3009027 | 0.004116 | 0.829332 | 0.90173 |
| **GCC$_{acidic}$** | | | 83.19467554 | 0.004635 | 0.811854 | 0.84886 |
| **CCG** | | | 73.47538575 | 0.004861 | 0.804469 | 0.78778 |

| Adsorbent | Isotherms | Metals | i/n | kf | R2 |
|---|---|---|---|---|---|
| **GCC$_{MnOx}$** | Langmuir | Pb | 0.54829 | 7.19913 | 0.98776 |
| **GCC$_{FeOx}$** | | | 0.65775 | 3.532482 | 0.9764 |
| **GCC$_{alkaline}$** | | | 0.62423 | 4.420791 | 0.98165 |
| **GCC$_{oxidic}$** | | | 0.75956 | 1.626447 | 0.95794 |
| **GCC$_{acidic}$** | | | 0.76393 | 0.910395 | 0.97151 |
| **CCG** | | | 0.73778 | 1.124786 | 0.98768 |
| **GCC$_{MnOx}$** | Langmuir | Cd | 0.73596 | 1.131019 | 0.98656 |
| **GCC$_{FeOx}$** | | | 0.77523 | 0.847442 | 0.97516 |
| **GCC$_{alkaline}$** | | | 0.70874 | 2.447147 | 0.95625 |
| **GCC$_{oxidic}$** | | | 0.74579 | 1.134201 | 0.98743 |
| **GCC$_{acidic}$** | | | 0.77575 | 0.773001 | 0.9682 |
| **CCG** | | | 0.75458 | 0.663819 | 0.93721 |
| **GCC$_{MnOx}$** | Langmuir | Cu | 0.72664 | 1.261159 | 0.98687 |
| **GCC$_{FeOx}$** | | | 0.76795 | 0.802749 | 0.9735 |
| **GCC$_{alkaline}$** | | | 0.75286 | 1.710882 | 0.95644 |
| **GCC$_{oxidic}$** | | | 0.75697 | 0.792392 | 0.9632 |
| **GCC$_{acidic}$** | | | 0.74384 | 0.746054 | 0.94186 |
| **CCG** | | | 0.73769 | 0.695921 | 0.92382 |

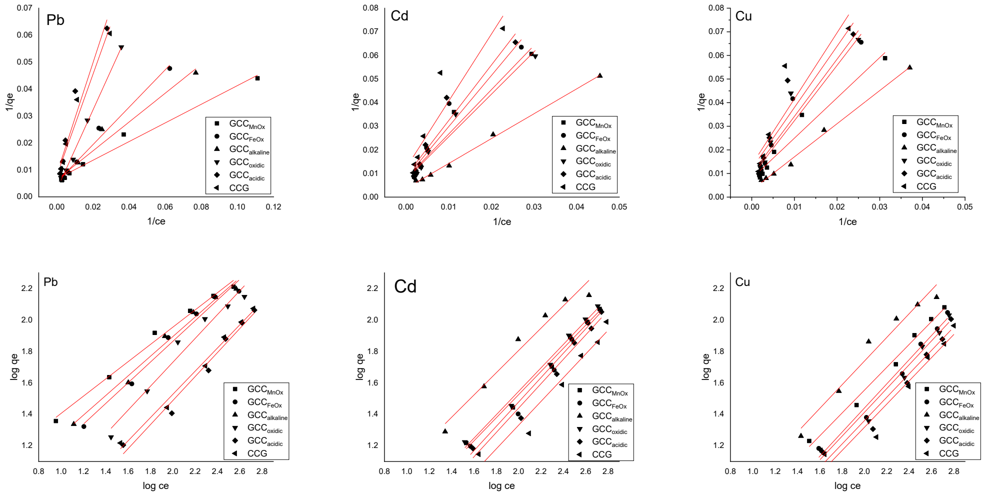


**Figure 8** Langmuir's and Freundlich's isotherm plots for the adsorption of Cu, Cd and Pb metals into CCG and (GCC$_{acidic}$), (GCC$_{alkaline}$), (GCC$_{oxidic}$), (GCC$_{MnOx}$), and (GCC$_{FeOx}$).

### Kinetic study

Adsorption kinetics is an important feature to describe the adsorption efficiency and provides useful information about the adsorption mechanism of the adsorbate on the adsorbent [22]. The maximal adsorption of Cu, Cd and Pb metals into CCG and (GCCacidic), (GCCalkaline), (GCCoxidic), (GCCMnOx), and (GCCFeOx) adsorption was observed. Fast adsorption in first 10 min, which reached equilibrium in 45 min it shows in **Figure 9** Based on the fast kinetic behavior of the adsorption process, it appears that an active site was available on CCG and (GCCacidic), (GCCalkaline), (GCCoxidic), (GCCMnOx), and (GCCFeOx) for removal of Cu, Cd and Pb metals absorption. A 45-min incubation eventually reached dynamic equilibrium after the adsorbent surface became saturated with adsorbate. Further analyzing the kinetic characteristics of Cu, Cd and Pb metals adsorption into CCG and (GCCacidic), (GCCalkaline), (GCCoxidic), (GCCMnOx), and (GCCFeOx) by utilizing pseudo 1st and 2nd order kinetic equations was carried out. As results both kinetic models ware fit data with linear regression of Cu, Cd and Pb metals equilibrium in **Table3**. It shows 1st order kinetic model R2 value with linear regression for Cu, Cd and Pb metal into CCG and (GCCacidic), (GCCalkaline), (GCCoxidic), (GCCMnOx), and (GCCFeOx) every adsorbent, value bellow (R2 > 75). 2nd order kinetic model R2 value with linear regression for Pb metal into CCG and (GCCacidic), (GCCalkaline), (GCCoxidic), (GCCMnOx), and (GCCFeOx) every adsorbent, value between (R2 < 91 - 99). For Cd and Cu metal R2 value into CCG and (GCCacidic), (GCCalkaline), (GCCoxidic), (GCCMnOx), and (GCCFeOx) adsorbent value between (R2 < 93 - 96).

**Table 3** Pseudo 1st and 2nd order kinetic model for the removal of Cu, Cd and Pb metals by CCG and (GCCacidic), (GCCalkaline), (GCCoxidic), (GCCMnOx), and (GCCFeOx).

| Adsorbent | Kinetics parameters | metals | Qe(mg/g) | Kl | Rl |
|---|---|---|---|---|---|
| **GCC$_{\mathrm{MnOx}}$** | pseudo 1st | Pb | 27.63823 | −0.00068 | 0.58987 |
| **GCC$_{\mathrm{FeOx}}$** | | | 35.29531 | −0.00078 | 0.62006 |
| **GCC$_{\mathrm{alkaline}}$** | | | 25.96995 | −0.00067 | 0.59521 |
| **GCC$_{\mathrm{oxidic}}$** | | | 37.84883 | −0.00071 | 0.5595 |
| **GCC$_{\mathrm{acidic}}$** | | | 35.25721 | −0.0007 | 0.56169 |
| **CCG** | | | 40.06247 | −0.00079 | 0.59991 |
| **GCC$_{\mathrm{MnOx}}$** | pseudo 1st | Cd | 40.99746 | −0.00081 | 0.72601 |
| **GCC$_{\mathrm{FeOx}}$** | | | 48.13647 | −0.00087 | 0.77179 |
| **GCC$_{\mathrm{alkaline}}$** | | | 47.23192 | −0.00083 | 0.72472 |
| **GCC$_{\mathrm{oxidic}}$** | | | 43.55088 | −0.00082 | 0.72477 |
| **GCC$_{\mathrm{acidic}}$** | | | 42.50748 | −0.00082 | 0.72471 |
| **CCG** | | | 34.48036 | −0.00088 | 0.74631 |
| **GCC$_{\mathrm{MnOx}}$** | pseudo 1st | Cu | 39.16408 | −0.00079 | 0.60737 |
| **GCC$_{\mathrm{FeOx}}$** | | | 33.38645 | −0.00069 | 0.56443 |
| **GCC$_{\mathrm{alkaline}}$** | | | 36.00832 | −0.00072 | 0.52127 |
| **GCC$_{\mathrm{oxidic}}$** | | | 36.11217 | −0.00078 | 0.60899 |
| **GCC$_{\mathrm{acidic}}$** | | | 28.17373 | −0.00078 | 0.57159 |
| **CCG** | | | 26.6415 | −0.00067 | 0.58963 |
| **Adsorbent** | **Kinetics parameter** | **metals** | **Qe(mg/g)** | **K2** | **R2** |
| **GCC$_{\mathrm{MnOx}}$** | pseudo 2nd | Pb | 172.7116 | 0.001173 | 0.99262 |
| **GCC$_{\mathrm{FeOx}}$** | | | 166.9449 | 0.00079 | 0.98373 |
| **GCC$_{\mathrm{alkaline}}$** | | | 167.5042 | 0.001213 | 0.9918 |
| **GCC$_{\mathrm{oxidic}}$** | | | 161.0306 | 0.000521 | 0.96477 |
| **GCC$_{\mathrm{acidic}}$** | | | 140.056 | 0.000415 | 0.91457 |
| **CCG** | | | 142.2475 | 0.000421 | 0.92623 |
| **GCC$_{\mathrm{MnOx}}$** | pseudo 2nd | Cd | 135.8696 | 0.000576 | 0.96248 |
| **GCC$_{\mathrm{FeOx}}$** | | | 135.6852 | 0.000491 | 0.94813 |

| | | | | |
|---|---|---|---|---|
| **$GCC_{alkaline}$** | | 163.9344 | 0.000525 | 0.96689 |
| **$GCC_{oxidic}$** | | 144.0922 | 0.000487 | 0.95284 |
| **$GCC_{acidic}$** | | 133.5113 | 0.000489 | 0.94713 |
| **CCG** | | 116.8224 | 0.000543 | 0.93549 |
| **$GCC_{MnOx}$** | Cu | 135.8696 | 0.000576 | 0.96248 |
| **$GCC_{FeOx}$** | | 135.6852 | 0.000491 | 0.94813 |
| **$GCC_{alkaline}$** | | 163.9344 | 0.000525 | 0.96689 |
| **$GCC_{oxidic}$** | | 144.0922 | 0.000487 | 0.95284 |
| **$GCC_{acidic}$** | | 133.5113 | 0.000489 | 0.94713 |
| **CCG** | | 116.8224 | 0.000543 | 0.93549 |

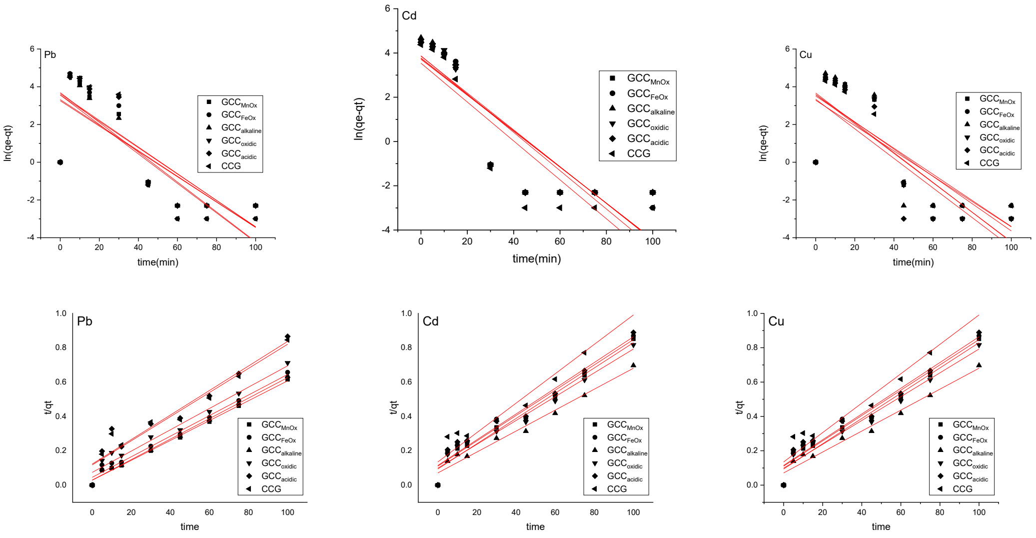


**Figure 9** pseudos' 1st and 2nd order kinetic model for the adsorption of Cu, Cd and Pb into CCG and ($GCC_{acidic}$), ($GCC_{alkaline}$), ($GCC_{oxidic}$), ($GCC_{MnOx}$), and ($GCC_{FeOx}$).

### Adsorption comparison of mixed metals conditions

Comparison investigated of The uptake maxed condition (Cu, Pb, and Cd) metals by CCG and (GCCacidic), (GCCalkaline), (GCCoxidic), (GCCMnOx), and (GCCFeOx) from an aqueous solution. In a 100 mL flask with a 50 mL of condiment at optimum pH, adsorbent dosage of 4 g/L, metals concentration of 100 mg/L, adsorption period 45 min, at a temperature of 30 °C at 180 rpm. Competitive adsorption between heavy metals in max condition actively on the surface and function group of every modified GCC and unmodified GCC in **Figure 10** shows that CCG modified by MnOx with the Cu 35.6 mg/L, Cd 21 mg/L, and Pb 16.5 mg/L, and FeOx with the Cu 28 mg/L, Cd 23.5 mg/L and Pb 13.1 mg/L, better than the other modified adsorbents. Other adsorbents by Orders GCCalkaline Cu 22.6 mg/L, Cd 23.1 mg/L and Pb 16.7 mg/L, GCCoxidic Cu 19.3 mg/L, Cd 19.7 mg/L, and Pb 18 mg/L, GCCacidic Cu 15.5 mg/L, Cd 16.2 mg/L, and Pb 14.6 mg/L, and GCC Cu 15 mg/L, Cd 11.1 mg/L and Pb 14.9 mg/L. according to result in GCCMnOx is not only in a single condition also in a maxed condition also suitable for heavy metals adsorption because of improvement in their surface and functions group. Competition between Cu, Pb, and Cd metals in max condition shows that Pb has more Desire than Cu and Cd metals despite having similar adsorption conditions. As a total adsorb by adsorbents CCG 40.4 mg/L, GCCacidic 45.2 mg/L, GCCalkaline 61 mg/L, GCCoxidic 56.5 mg/L, GCCMnOx 72.4 mg/L, and 64.7 mg/L for GCCFeOx, is very less than adsorb by adsorbent in single metal condition.

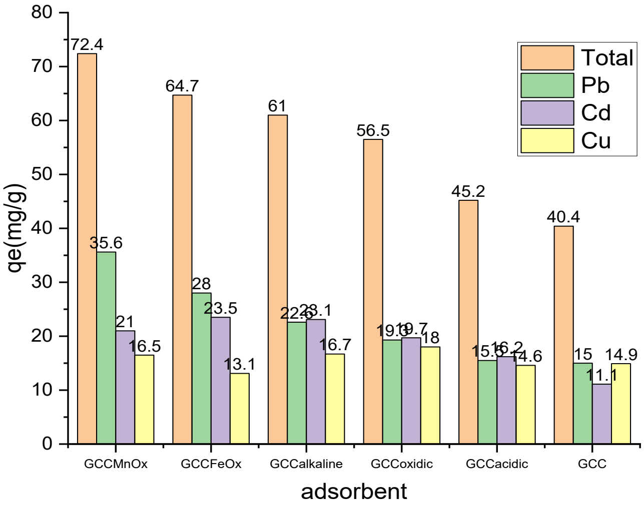


**Figure 10** adsorption of maxed metals (Cu, Cd and Pb ions) condition into CCG and (GCCacidic), (GCCalkaline), (GCCoxidic), (GCCMnOx), and (GCCFeOx).

## Conclusions

Much has been done in the field of absorbing heavy metals by adsorbents, and to increase the strength of adsorbents, chemical substances have been used, but the basic problem is to find out which chemical substances are better and which physical and chemical changes occur in the adsorbents. In summary, GCC was synthesized by modification with (acidic), (alkaline), (oxidic), (MnOx), (FeOx). via surface grafting. The obtained GCCMnOx exhibited good adsorption capacity for Pb and GCCalkaline for Cd and Cu. And the maxed condition (GCCMnOx), (GCCFeOx) was slightly better than other adsorbents. The suitable pH for all adsorbent in range of pH5 and pH6, after 45 min all adsorbent all most reach the equilibrium, with the increasing metals concentration adsorption capacity also increased. For well known the physicochemical properties of the adsorbent we use (XRF), (FT-IR), (XRD), (SEM-EDX), and (BET). After modification of adsorbents surface area as well as functional groups (hydroxyl group, and Manganese oxide group) improved. Spicily GCC modified MnOx and alkaline. The adsorption of Cu, Cd and Pb metals could be well expressed by Freundlich and Langmuir model. Which is Langmuir model better than the Freundlich model. Process followed by pseudo-second-order and pseudo-first-order kinetic curves which is pseudo-second-order better than pseudo-first-order. As result Coal gangue modified with MnOx and alkaline improves their functions group and surface area and better for heavy metals removal and the worst was modified Coal gangue with Acidic.

## References

[1] ME Mahmoud, GM Nabil, MM Zaki and MM Saleh. Starch functionalization of iron oxide by product from steel industry as a sustainable low cost nanocomposite for removal of divalent toxic metal ions from water. *Int. J. Biol. Macromol.* 2019; **137**, 455-68.

[2] WW Tang, GM Zeng, JL Gong, J Liang, P Xu, C Zhang and BB Huang. Impact of humic/fulvic acid on the removal of heavy metal ls from aqueous solutions using nanomaterials: A review. *Sci. Total Environ.* 2014; **468**, 1014-27.

[3] AE karkouri, K Harboul, H Arroud and ME Hassouni. Hexavalent chromium removal from a tannery effluent by a bacterial consortium. *Moroccan J. Chem.* 2019; **7**, 615-23.

[4] AB Duwiejuah, SJ Cobbina and N Bakobie. Review of eco-friendly biochar used in the removal of trace metals on aqueous phases. *Int. J. Environ. Bioremediation Biodegradation* 2017; **5**, 27-40.

[5] M Hamed, IM Ahmed and SS Metwally. Adsorptive removal of methylene blue as organic pollutant by marble dust as eco-friendly sorbent. *J. Ind. Eng. Chem.* 2014; **20**, 2370-7.

[6] J Yan, G Lan, H Qiu, C Chen, Y Liu, G Du and J Zhang. Adsorption of heavy metals and methylene blue from aqueous solution with citric acid modified peach stone. *Separ. Sci. Tech.* 2018; **53**, 1678-88.

[7] I Anastopoulos and GZ Kyzas. Composts as biosorbents for decontamination of various pollutants: A review. *Water Air Soil Pollut.* 2015; **226**, 61.

[8] AE Burakov, EV Galunin, IV Burakova, AE Kucherova, S Agarwal, AG Tkachev and VK Gupta. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treat- ment purposes: A review. *Ecotoxicol. Environ. Saf.* 2018; **148**, 702-12.

[9] WW Ngah, LC Teong and MM Hanafiah. Adsorption of dyes and heavy metal ions by chitosan composites: A review. *Carbohydr. Polymer.* 2011; **83**, 1446-56.

[10] J Ma, X Wang, Q Fu, Y Si, J Yu and B Ding. Highly carbonylated cellulose nanofibrous membranes utilizing maleic anhydride grafting for efficient lysozyme adsorption. *ACS Appl. Mater. Interfac.* 2015; **7**, 15658-66.

[11] BJ Ni, QS Huang, C Wang, TY Ni, J Sun and W Wei. Competitive adsorption of heavy metals in aqueous solution onto biochar derived from anaerobically digested sludge. *Chemosphere* 2019; **219**, 351-7.

[12] S Li, S Harris, A Anandhi and G Chen. Predicting biochar properties and functions based on feedstock and pyrolysis temperature: A review and data syntheses. *J. Cleaner Prod.* 2019; **215**, 890-902.

[13] B Ahmed, JL Zhou, HH Ngo, W Guo and M Chen. Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. *Bioresource Tech.* 2016; **214**, 836-51.

[14] H Li, X Dong, EBD Silva, LMD Oliveira, Y Chen and LQ Ma. Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. *Chemosphere* 2017; **178**, 466-78.

[15] I Inyang, B Gao, Y Yao, Y Xue, A Zimmerman, A Mosa, P Pullammanappallil, YS Ok and X Cao. A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. *Crit. Rev. Environ. Sci. Tech.* 2016; **46**, 406-33.

[16] J Wu, T Wang, J Wang, Y Zhang and WP Pan. A novel modified method for the efficient removal of Pb and Cd from wastewater by biochar: Enhanced the ion exchange and precipitation capacity. *Sci. Total Environ.* 2021; **754**, 142150.

[17] T Chen, Y Zhang, H Wang, W Lu, Z Zhou, Y Zhang and L Ren. Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. *Bioresource Tech.* 2014; **164**, 47-54.

[18] H Wu, Q Feng, H Yang, E Alam, B Gao and D Gu. Modified biochar supported Ag/Fe nanoparticles used for removal of cephalexin in solution: Characterization, kinetics and mechanisms. *Colloid. Surface. Physicochem. Eng. Aspect.* 2017; **517**, 63-71.

[19] T Sizmur, T Fresno, G Akgül, H Frost and E Moreno-Jiménez. Biochar modification to enhance sorption of inorganics from water. *Bioresource Tech.* 2017; **246**, 34-47.

[20] H Lu, W Zhang, Y Yang, X Huang, S Wang and R Qiu. Relative distribution of $Pb^{2+}$ sorption mechanisms by sludge-derived biochar. *Water Res.* 2012; **46**, 854-62.

[21] A Sari, M Tuzen, OD Uluözlü and M Soylak. Biosorption of Pb (II) and Ni (II) fromaqueous solution by lichen (Cladonia furcata) biomass. *Biochem. Eng. J.* 2007; **37**, 151-8.

[22] LG Boutsika, HK Karapanagioti and ID Manariotis. Aqueous mercury sorption by biochar from malt spent rootlets. *Water Air Soil Pollut.* 2014; **225**, 1805.