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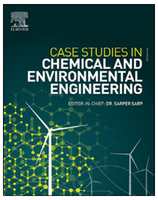

Influence of pyrolyzed sludge use as an adsorbent in removal of selected trace metals from wastewater treatment

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ABSTRACT

The disposal of sludge processes accounts for *60%* of the total operation and *40%* of total emissions of greenhouse gas from wastewater treatment plants operations. Moreover, sludge contains pathogenic microorganisms, organics, inorganics, trace metals and emerging micropollutants, which can be a public health menace. To comply with the Environmental Protection Agency standards, sludge must be stabilized and detoxified before being disposed or reused. This study focuses on the use of sludge biochar *(adsorbent)* from the pyrolysis of wastewater treatment sludge for the removal of selected trace metals *(copper, cobalt and nickel)* in aqueous solution by optimization of the temperature and adsorbent particle sizes. The morphology of the surface at increased temperature *(400, 500 and 600 °C)* showed an enhanced surface with space and structure (pores) that promoted the adsorption of metal ions. A decreased of adsorbent particle size from 250 μm to 100 μm and an increased in pyrolyzed biochar temperature from *(400, °C, 500 °C and 600 °C)* resulted in the removal of the trace metals (*77.86%, 75%* and *56.25%* of copper, cobalt and nickel respectively) from the aqueous solution. Biochar produced from sludge can be an alternative adsorbent for the removal of trace metal in wastewater treatment processes.

1. Introduction

The growth of industrialization, urbanization, population increase together with the significant growth of modern zones *(fourth industrial revolution)*, has increased issues related to sludge disposal and strict requirements to achieve effluent permissible limits for the treatment of wastewater. Wastewater streams contain organic, inorganic, trace metals and micropollutants from the wastewater treatment processes units. Sludge treatment is considered one of the most important and emerging issues in wastewater treatment, owing to the high demand for energy and high costs related to its treatment [1–4. The removal of organic, inorganic, trace metals, micropollutants and the treatment of industrial effluents are done through a series of processes *(chemical, physical and biological)* in a wastewater treatment plant [5]. Currently, there are environmental concerns associated with the generation of sludge in developed and developing countries [5]. Many concerns have been raised with regards to sewage sludge disposal due to the rapid evolution of industries and rapid urbanization [5]. This is because sewage sludge contains toxic contaminants and pathogens that are potentially harmful to human health and detrimental to the environment [6]. Trace metals contaminants can hardly biodegrade and gradually accumulates in the environment. They can cause serious health and environment problems to becoming ecotoxicological hazard if not properly treated. Beyond the threshold, toxic metals such as nickel, copper and cobalt pose serious damages to human health such as chronic, nervous system, loss of organic function and acute poisoning [7]. It is a great demand to eliminate these metals ions before discharge. Some of the established wastewater treatment process are; membrane filtration, chemical precipitation, electrochemical reaction, coagulation and flocculation, ion-exchange, oxidation and ozonation, adsorption and reverse osmosis. Natural adsorption emerged as the most promising technology due to its applicability, versatility, economic feasibility, non-by-product generation and low toxic [8,9]. Activated carbon is the most prevailing adsorbent because of the high adsorption capacity, high surface area, and high degree of the surface reactivity, however, it must be regenerated and it is much expensive. Biomaterials support more advantages than activated carbon that includes cheaper synthesised organic and inorganic, the chelating group with high concentration and better mechanical stability

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[10]. This is with an advanced strategized novel engineered nano-material (bio-sorbent). To fulfil this study gap, a sludge absorbent prepared using a range of pyrolysis temperature and particle sizes are utilized with ultra-adsorptive performance and effectiveness.

1.1. *Wastewater treatment processes*

Wastewater is the fluid waste from domestic and industrial usages. The wastewater treatment units comprise of the following: Screening; is the unit where course debris *(screens etc.)* are removed. Primary treatment; is unit where sludge is separated from wastewater using a primary clarifier. Secondary treatment; this comprises of the activated sludge or the biofilm process where nutrients are removed. Final treatment *(tertiary);* this is the stage where the pathogens are eliminated *(disinfection)* [11].

The sludge produced contains biomass and microbial cells from the wastewater processes. The insight of the wastewater treatment characteristics of secondary sewage sludge, dewatered activated sludge, primary sludge, mixed primary and secondary sludge and raw sludge are 4195 mg/l (pH of 6.46), 158.31 mg/l (pH 7.82), 30.50 mg/L (pH of 7.20), 4510 mg/L (pH of 6.61) and raw sludge dependent with the source respectively [12].

Synman and Herselman, *(2006)* [13] reported that sludge management is still a major concern in South Africa. The conventional ways of sludge disposal include utilization in combustion, anaerobic digestion *(AD)*, landfilling, and agronomy as organic fertilizer [5]. Sludge has been also used as a great source of energy in incineration, pyrolysis, gasification, *AD etc.,* [13]. This is because of the organic content that amounts to approximately *60%* in a dry matter [5]. In addition to this, gas obtained from sludge can also be used as a source of energy *(biomethane)* since the heating value is reduced after the reduction of organic compounds in sludge *(after anaerobic digestion)* during biological biomass conversion [5].

1.2. *Sludge treatment and disposal*

Sludge is the residue *(solid)* from wastewater treatment. It is potentially harmful since it contains organic, inorganic, trace metals, harmful microorganisms and other toxic pollutants which could be a public health menace. Rapid modernization in conjunction with rapid industrialization in most developed countries has led to an increase in sludge production. The treatment of sludge is therefore considered a major concern in wastewater treatment facilities: *60%* of the operating cost of the most wastewater treatment facility is allocated to the disposal of sludge and costs related to its treatment [14].

To comply with the environmental protection criteria, sludge from wastewater treatment must be detoxified and stabilized before its final disposal or application. Besides the traditional methods, like landfilling, land application after dry bed, ocean dumping, thermochemical *(i.e. incineration, pyrolysis, gasification)* and biological *(i.e. anaerobic digestion, aerobic and composting)* technologies have been developed for sludge treatment and minimization.

1.2.1. *Biological treatment of sludge*

Traditional methods for sludge disposal have restrictions around the land application of sewage sludge since they contain toxic organics, inorganics and trace metals that are harmful to the living organisms [15]. Incineration, on the other hand, generates an amount of ash which can only be disposed of in landfills due to the number of toxic substances they contain. Land applications are facing restrictions due to the shortage of available land space along with the strict regulations around the permissible effluent limits [15]. Due to strict environmental laws related to traditional disposal methods, biological treatment has drawn much attention among researchers. Composting, aerobic and *AD* methods are widely used to remove toxic substances, pathogenic microorganisms and to reduce the sludge volume and sludge stabilization [14]. The minimization and stabilization of sewage sludge is a major concern in most wastewater treatment. Anaerobic digestion is one of the biological processes used in the stabilization of sludge. It covers the thickening and dewatering of sludge in a reactor with an aeration system. The level of degradation in this process depends on the hydraulic and sludge retention time, temperature, *C/N* ratio, *pH,* system temperature among other parameters. Anaerobic digestion can be achieved under mesophilic and thermophilic temperatures [14].

Anaerobic digestion is reported to be effective in terms of cost since energy can be recovered from biomethane with less impact on the environment. It is used in most of the sewage treatment facilities at full scale. This technology is an essential stabilization system in modern wastewater treatment plants. It assists in the decomposition of organic matter into biogas with *60%* bio-methane content. It degrades solids and reduces the number of pathogenic substances. Although anaerobic digestion provides quite a lot of advantages, there are some disadvantages associated with this technology *i.e.* relatively slow process, the complex materials require a long residence time, long hydrolysis step, requires large bio-reactor volume [14].

The other process used for the stabilization of sludge is composting. It is often used for the treatment of complex waste whose stabilized product could be used as organic fertilizer. Composting is operated under aerobic conditions where the aeration facilitates the hydrolysis of complex substances into simple ones, due to the enzyme production and increase in the rate of growth microorganisms. It is achieved in three stages related to temperature evolution. During the first stage, the temperature of the system is increased due to the growth of mesophilic microbiota. The second stage is facilitated by the increase in temperature which activates the thermophilic microbiota and kills most of the pathogens. In the third phase, a decrease in temperature results in the activation of mesophilic microbiota. However, this process requires an additional bulking agent such as sawdust. Composting is a stabilization process whose limitations are the loss of temperature, the presence of unstable substances and pathogens, *etc.,* [14].

1.2.2. *Thermochemical treatment: pyrolysis process*

Although many researchers have been focusing on finding pretreatment methods for the minimization of sludge, a certain quantity of sludge is still produced at the end of the day. Since a zero waste *(sludge)* is practically not feasible, hence, there is a need for post-treatment of sludge within the wastewater sector [16]. The thermochemical sludge technology such as pyrolysis has been getting attention among researchers due to the variety of by-products it generates. Pyrolysis is a process during which biomass *(sludge)* is heated at high temperatures in the absence of oxygen to generate syngas, biochar and bio-oil [6]. Hossain et al., *(2011)* [17] reported that the minimization of sewage sludge can be done in an ecologically and cost-effectively manner through the conversion of sewage sludge by pyrolysis. Biochar, the solid by-products of pyrolysis, is a type of black carbon which usually contains traces of polyaromatic carbon, elemental and graphitic carbon. It has been found useful in the restoration of destroyed soil, in the improvement of crop yield as well as adsorbents of contaminants. Chen et al., *(2014)* [18] report that the properties *(chemical and physical)* of the biochar obtained after pyrolysis depend on the conditions of pyrolysis where temperature, among other conditions, is an important factor that influences the characteristics of the biochar and bio-oil.

Pyrolysis is conducted to enhance the porosity of the material being treated. The decomposition reaction leads to the improvement of organic functional groups that remain with a carbonaceous skeleton. Chen et al., *(2014)* [18] observed that the pyrolysis temperature increase leads to a decrease in the wavelength of the *FTIR* peaks. It simply indicates that the decomposition of chains of hydrocarbon takes place during pyrolysis and that the functional groups of oxygen are reduced leaving the structure that provides π-electrons, strong bond with the cation of trace metals.

The trace metal removal capacity by use of biochar was also observed and varies depending on pore size, pore-volume, surface area and fractal dimension. The efficiency removal is directly proportional to the increase in pyrolysis temperature on biochar preparation. It has been reported that an increase in fractal dimension indicates that pyrolysis temperature enhances the porosity of the biochar. When the biochar derived from biomass is activated, it exhibits a higher adsorption capacity as compared to commercialized activated carbon [18]. A study conducted by Chen et al., *(2014)* [18] reported that *2*.5 mg of activated carbon can have a maximum removal capacity of trace metals in wastewater.

Hence, it is very important to determine the relationship between the pyrolysis temperature and the properties of the biochar. Several studies have been conducted and yet the uncertainty as to what is the ideal or optimal temperature for pyrolysis remains a key question on how it affects biochar pore size, pore-volume, surface area and fractal dimension [18]. Zielińska, A. and P. Oleszczuk *(2015)* reported that the pyrolytic conversion of sewage sludge into biochar enhances the removal of a considerable number of contaminants in the sludge. They further claim that trace metals bioavailability and ease of motion is decreased in biochar in comparison with unprocessed sewage sludge [19]. It has also been reported that biochar from sewage sludge contains a relatively high amount of minerals and elemental carbon. The biochar is also said to have a high number of cations which could be exchanged and has high porosity. Hence, it can be used for the removal of contaminants from wastewater [19]. Since activated carbon, the most used material for contaminants removal, is reported to be quite expensive, biochar derived from the readily available material such as sewage sludge is becoming an alternative adsorptive material to inexpensive processes [19].

Adsorbents are, amongst other application, used for the purification of water. Sand is mostly used in the most filtration system. Owing to the limitations of sand to remove some contaminants, filters with multiple layers and various substances are used to trap contaminants. Coal is mostly used in such multiple layer system, but its high cost and unsustainability leave room for improvement [19]. Hence, Zielińska, A. and P. Oleszczuk *(2015)* [19] reported that using waste from industrial sectors could lead to the development of cost-effective and reliable water treatment techniques.

Praspaliauskas and Pedišius, *(2017)* [5] reported that the use of sludge as fertilizer is a method which is no longer supported or allowed. Sludge is collected throughout the year while the soils need to be fertilized only once or twice a year. Therefore, the collected sludge must be kept until future use, which brings the same environmental menace and headspace costs. In addition to that, a hindrance to the use of sludge in agriculture has led to an important decrease in the usage of sewage sludge in the agricultural sector [5].

The trace metals from sludge are still found in the ashes which are released into the atmosphere along with exhaust gases *(fly ashes)*. These necessitate a proper treatment of the exhaust gases for the reduction of trace metals pollution since exhaust gases must comply with environmental regulations. This method is partially inefficient and therefore less preferred [5]. A wide gap of research is open in utilization, beneficiation and handling of sludge in most developed and developing countries. Several alternatives have been developed for sludge minimization and utilization. Amongst other techniques, pyrolysis of sludge has been reported to be a cost-effective and clean method [18].

Pyrolysis of sludge, unlike other methods, focuses on the recycling of valuable fuel substances *(hydrocarbon)* while decreasing the amount of solid waste [18]. Among the various techniques developed for the utilization of the wastewater residue, the production of biochar through pyrolysis to treat the very same wastewater has been reported to be economical and effective for the industrial effluent treatments. The most common substance used in the treatment of wastewater is activated carbon [20]. However, it is being rapidly replaced by other carbonaceous materials *(agricultural waste, sludge, etc.,)* because they are readily available and affordable.

Biochar, the solid by-products of pyrolysis, is a type of black carbon which usually contains traces of polyaromatic carbon, elemental and graphitic carbon. It has been found useful in the restoration of destroyed soil, in the improvement of crop yield as well as an adsorbent of contaminants [6]. Based on the principle of treating waste by waste, biochar from sludge, like any other type of adsorbent, has been found useful for the treatment of wastewater. Effluents from various industries contain a wide variety of pollutants which are detrimental to the environment. Hence, there is a need to treat them before releasing to the water body. Aslan, *(2016)* [6] reported that the environmental pollution problems which affect the aquatic system, as well as the soil, is caused by trace metals in effluents. Since trace metals contained in industrial effluents are considered a threat to the environment, researchers have been focusing on techniques to remediate this problem [6].

Various techniques for the removal of trace metals from aqueous solution are reverse osmosis, oxidation, precipitation, ions exchange, filtration, and adsorption. These techniques have been reported to be expensive and inefficient in cases where the water contains trace metals in extremely low levels [6,21]. Hence, new methods have been investigated to treat wastewater. Adsorption is reported to be the preferred process for the removal of trace metals in very low concentrations [6,21]. Activated carbon is the most used adsorbent in the adsorption process. Due to the fact that the use of activated carbon is expensive, the use of readily available, less expensive alternatives such as sludge has been investigated [6,22]. Although commercialized activated carbon possesses better physical properties *(high surface area, high pore volume)* than those of biochar, the capability of biochar *(from sludge)* to adsorb both organic pollutants and trace metals has been reported to be quite similar or even better than those of activated carbon [5,6]. The other advantage of biochar from sludge, as an adsorbent, is that the process is done at a relatively low cost since no activation is required [6,18]. Hence, this study will focus on the use of pyrolysis by-products *(biochar)* from sludge as an environmentally friendly process for wastewater treatment. The biochar will act as an innovative adsorbent for the treatment of wastewater utilizing sludge disposal.

1.3. Sludge pyrolysis parameters

Parameters such as temperature, residence time and particle size have a direct effect on the quality of biochar. Chen et al., *(2014)* [18] reported that the properties *(chemical and physical)* of the biochar obtained after pyrolysis depend highly on the conditions of pyrolysis.

1.3.1. Pyrolysis temperature

Temperature has been reported to be the most important parameter in the pyrolysis process. It has a considerable effect on biochar quality. Agrafioti et al., *(2013)* [12] reported that an increase in pyrolysis temperature beyond optimum leads to a decrease in the yield of biochar. A yield decrease of *32%* was observed from $300\ ^{o}C$ to $500\ ^{o}C$ which can be justified by the first decomposition of the dry feed and the second decomposition of the solid product [12]. A similar trend was observed by Hossain et al., *(2011)* [17].

Pyrolysis temperature also affects the *pH* of the biochar. Hossain et al., *(2011)* [17] observed that low pyrolysis temperature favours acidic *pH* whereas biochar subjected to high temperature was alkaline. A similar observation was made by Agrafioti et al., *(2013)* [12], they concluded that biochar obtained at low temperature was appropriate for agricultural applications whereas that obtained at high temperature was suitable for the removal of pollutants due to the highly porous structure developed. Hence, the ideal pyrolysis temperature depends highly on biochar future applications [17]. Besides the effect it has on *pH* and the yield, increasing pyrolysis temperature reduces the amount of nitrogen, the capacity of water sorption and the capacity of cation exchange whereas the stability of heavy and carbon content increases [10].

To make sure of the trace metal stability, Agrafioti et al., *(2013)* [12] performed a toxicity characteristic leaching procedure on sludge as well as the obtained biochar to assess the possibility of contaminants transfer to a liquid medium. Their findings revealed that the transfer of trace metals from biochar was not considered since their range was between zero *(0)* and *0.*74 mg/kg whereas that of the raw material *(sludge)* was between zero *(0) to 5*.5 mg/kg*)* [12].

The pyrolysis temperature also influences the *BET* surface area. An increase in the temperature results in an increase in surface area. An increase of $13.92\ m^2$ has been observed by Agrafioti et al*., (2013)* [12] from a temperature of $300\ ^oC$–$500\ ^oC$. This behaviour is attributed to the fact that the chemical structure of the sludge *(feed)* was altered during pyrolysis. Furthermore, increasing the temperature of pyrolysis results in an improvement of the aromaticity of the sludge, which promotes the formation of mesopores and micropores thus a high surface area is observed. However, the formation of mesopores and micropores is hindered by the high content of the feed *(sludge)*. Hence, the characteristics of sludge, at any rate, determines the quality of the biochar [12].

1.3.2. Residence time

The other factor that influences the quality of biochar is residence time. However, in the studies done by Agrafioti et al*., (2013)* [12] showed that the residence time did not have a much significant effect on the yield of biochar on as there was no considerable yield change among samples pyrolyzed at the same temperature for *30, 60* and 90 min.

This study aimed to utilize biochar generated from wastewater treatment sludge in the purification of wastewater. The adsorptive performance of biochar from sludge produced under different temperature and particle size in the removal of trace metals *(Co, Cu and Ni)* was investigated. There are no studies for modified sludge as an adsorbent for selected trace metals removal *(Ni, Co, Cu)* under adsorbent modification at a pyrolyzed temperature of $400\ ^oC$, $500\ ^oC$ and $600\ ^oC$ and at a particle size of *100* and 250 μm.

2. Methodology

Sewage sludge was quantified and collected from a domestic wastewater treatment plant, Gauteng Province, South Africa. It was used for the generation of biochar, which served as an adsorbent in the experiment. The effect of pyrolysis temperature was assessed. The parameters *(temperature and adsorbent particle size)* were investigated for the trace metals *(copper, cobalt and nickel)* removal from aqueous solution (SM Figure A1).

2.1. Experimental procedure

2.1.1. Sample preparation and preliminaries analysis

The sludge was crushed in a cone crusher to reduce its size. It was then screened to obtain two different particle sizes: *100* and 250 μm. Thermogravimetric analysis *(TGA)* was conducted on the sample to assess its level of degradation. Fourier transform infrared spectroscopy *(FT-IR)* was used to evaluate the degradation rate and composting of the sample. The trace metal concentration of the wastewater was determined using Atomic Absorption Spectrometer (Thermo scientific ICE 3000 Series) and inductively coupled plasma-optical emission spectrometry *(ICP-OES) -(ICAP 6500 Duo, Thermo Scientific, UK)*. A solution of *0.*1 mmol of copper, cobalt and nickel was prepared with initial concentrations of 28 ppm.

2.1.2. Characterization of sludge

Sewage sludge characterization *(proximate and ultimate analysis)* was done to ascertain the composition. The proximate analysis consisted of the total solids *(TS%)*, moisture content *(MC%)* and volatile solids *(VS %)*. Total solids and moisture content of sludge at 20 g were analysed in triplicate using an oven for 24 hours at 105 °C. Volatile solids were analysed in triplicate using a furnace at 550 °C for 2 hours. The ultimate analysis consisted of elemental analysis of carbon, nitrogen, hydrogen, and sulphur *(CNHS)*. The proximate and ultimate analysis was in accordance to the *ASTM* D3173 *(moisture content), ASTM* D3302 *(total solids), ASTM* D3175 *(volatile solids)* and *ASTM* D3176-89 *(elemental analysis)* standard [23]. The pH of the sludge and metal ions were measured. Scanning electron microscope *(SEM)-(JSM 6360l VSEM, JEOM, Co, Japan)* and *X*-ray fluorescence *(XRF)-(Rigaku ZSX Primus II)* analysis were conducted on the sludge before pyrolysis to determine the chemical composition and to observe the surface morphology for the latter. Brunauer emmett teller *(BET)* analysis was conducted on the sludge to determine its surface area as well as its pore sizes and volume.

2.1.3. Biochar production using the pyrolysis process

The sludge was pyrolyzed in a furnace for 10 min. A set of samples (50 g each) was carbonized *(pyrolyzed)* in triplicate to assess the effect of temperature ($400\ ^oC$, $500\ ^oC$ and 600^oC) and particle size *(*100 μm *and* 250 μm*)* on the yield of biochar [5] and bio-oil as a by-product. The temperature variation was evaluated using *TGA-FT* on the degradation of the samples. The yield of biochar was calculated using Equation (1) [24].

$$Biochar\ Yield = \frac{m_{biochar}}{m_{sludge}} x100 \tag{1}$$

2.1.4. Characterization of biochar

Scanning electron microscope *(SEM)* and *X*-ray fluorescence equipment *(XRF)* analysis were conducted on the biochar after pyrolysis to determine the chemical composition and to observe the surface morphology for the latter. Brunauer emmett teller *(BET)* analysis was conducted on the biochar to determine its surface area as well as its pore sizes and volume.

2.1.5. Adsorption process

A *0.125 g* of the biochar *(*100 μm *and* 250 μm*)* obtained at *400, 500* and $600\ ^oC$ was mixed with different 100 mL of prepared solution of trace metals concentration. A prepared solution of *0.*1 mmol of copper, cobalt and nickel was used to investigate the adsorptive capacity of the biochar. A thermostatic agitator *(stirred batch adsorption systems)* at 200 rpm *(constant agitation rate)* was used to agitate the solutions for *10 hours* at both constant of $25\ ^oC$ and $30\ ^oC$ separately [5]. The batch solutions were filtered using a Buchner funnel. The metal concentration of both the wastewater and the filtrate was determined using *ICP-OES* and *AAS*.

2.2. Adsorption isotherm modelling

Adsorption isotherm was studied using Langmuir and Freundlich isotherm models at equilibrium. Langmuir isotherm model was used to predict the mono-layer adsorption surface of the active site. This involved the interaction between the trace metal ions and the absorbent by employing excel data fitting to the linear Langmuir model in Equation (2) [25,26].

$$\frac{C_e}{Q_e} = \left(\frac{1}{q_r}\right) C_e + \frac{1}{q_{r\ b}} \tag{2}$$

where Q_e was the adsorption capacity at equilibrium, q_r was the adsorption capacity of the maximum mono-layer, b was the Langmuir constant and was related to the energy of adsorption, C_e was the concentration of the metals at the equilibrium. The Langmuir parameters *(b and* q_r*)* and coefficient of determination *(*R^2*)* were determined from linearization plotting of Ce/Q_e Vs C_e.

Freundlich isotherm model was used to describe the multi-layer physio-chemical adsorption on a heterogeneous surface (Equation (3)) [26,27].

$$Log(q_e) = \frac{1}{n} Log(C_e) + Log(k_f) \tag{3}$$

where q_e was the adsorption capacity at equilibrium (mg/g), K_f was the

Freundlich constant that represented the adsorption capacity and adsorptive bond *(L/mg)*, *n* was the heterogeneity factor that represented the relative distribution and adsorption intensity of the energy and heterogeneity of the site of the adsorbate and C_e was the concentration of the liquid phase equilibrium *(mg/L)*. Freundlich parameters *(*K_f *and n)* and coefficient of determination (R^2) were determined from linearization plotting of Log (Q_e) *Vs* log (C_e).

The mass balance of copper, cobalt and nickel adsorbed *(qe)* and the efficiency removal *(R)* was determined using Equations (4) and (5) respectively [28].

$$q_e = \frac{Ci - Ce}{M_{adsorbent}} V_{solution} \tag{4}$$

$$R = \frac{Ci - Ce}{Ci} \tag{5}$$

where q_e was the capacity of adsorption, C_i was the initial concentration of the trace metal, C_e was the equilibrium concentration of the trace metals, $V_{solution}$ was the volume of the solution and $M_{adsorbent}$ was the mass of the adsorbent.

3. Results and discussions

3.1. Sewage sludge characterization

Sewage sludge characterization *(proximate and ultimate analysis)* was done to ascertain the composition. The proximate analysis consisted of the total solids *(TS%)*, moisture content *(MC%)* and volatile solids *(VS %)*. The ultimate analysis consisted of elemental analysis of carbon, nitrogen, hydrogen, and Sulphur *(CNHS)*. The pH of the sludge and metal ions were measured.

The moisture content of *37.16%* indicated less temperature required to remove water during the pyrolysis process. High total solids *(37.18%)* and volatile solids *(62.82%)* indicated a high organic content that gave a good thermo-chemical process. The *C, N, H* and *S* were *31.5, 2.81, 5.08* and *1.5* respectively. The carbon-nitrogen ratio of *11.2* indicated high carbon content that was converted to biochar with lesser pollutant compound formation like hydrogen sulphide and carbon monoxide. The pH of the sludge was found to be 7.02, copper 6.5, nickel 6.8 and cobalt 6.9. The pH of the solution in the adsorption process played a role of particle diffusion (hydrophobic interaction) that modify the concentration of the metal ions and shape (surface charge).

3.2. Degradation of the sludge

The thermal analysis (degradation) of the sludge was determined by the use of thermogravimetric analysis *(TGA)*, derivative thermogravimetry (DTG) and differential thermal analysis (DTA). This was the mass degraded *per* rate of change of temperature as showed in Fig. 1.

The degradation assisted in the determination of the optimum temperature of pyrolysis that was *200–650 °C* due to mass loss and evaporation of moisture content. The derivative thermogravimetry (DTG) indicated the gain/loss of the sample weight in the thermal transition. The differential thermal analysis (DTA) indicated the specific temperature of reaction at which the specific changes (phase transition) occurred within the sample (exothermic or endothermic) [29]. The devolatilization occurred at a threshold of 17.7 at biochar combustion mass%/min. This enhanced accuracy, efficiency and precision. The higher heating values and gross calorific values are thermodynamic conversions that helped determine the condition of biomass combustion [30,31].

3.3. Functional group analysis

Fourier transform infrared spectroscopy *(FT-IR)* was used to evaluate the degradation rate and composition of the sewage sludge. The main functional group of the raw sludge and activated sludge were characterised by *FT-IR* as shown in Fig. 2.

The composition of the sludge samples affected the shape of the *FT-IR* spectra. It reflected the chemical composition of the sample due to degradation processes [32]. Spectra reflected a strong intensity of 3940 cm^{-1} at the beginning of the analysis. This suggested that the compound was much affected by the activated sludge capacity and chemical composition. The intensity, shape and appearance nitrate band at 1186 cm^{-1} for *400, 500, 600 °C* was evident for sewage sludge-based compost maturity. The results show a fraction of aliphatic phosphates, aliphatic carboxylic acids, alkynes monosubstituted, aliphatic hydrocarbons and primary aliphatic alcohols. An increase in peak ratio was due to the decomposition of the sludge. There was a notable variation in relative intensity of the functional groups of the pyrolyzed sewage sludge using *FT-IR* spectra. The composition was supported by the activated sludge analysis library by Grube, M et al. (2005) [32] and Kowalski, M et al. (2018) [33]. The *FT-IR* analysis appeared to be useful in composition monitoring of activated sludge and provided a useful indicator for the change of sludge characteristics.

3.4. Biochar composition

The characterization of the biochar as a source of adsorbent from the pyrolyzed process is shown in Fig. 3. It was observed that the metals reduced in concentration with the optimization of different temperature. The *XRF* results revealed constant trace metals concentration with an increase in pyrolyzed temperature of the biochar production.

There was a significant decrease in the amount of *Fe* from *27.*4 mg/L to *16.*3 mg/L, *Ca* from *20.*5 mg/L to *14.*6 mg/L and *Si* from *3.*63 mg/L to *6.2, mg/L, P* from *11.*2 mg/L to *9.*4 mg/L, *Mg 2.*32 mg/L to *1.*51 mg/L, with lowest recorded at *Cr 0.*17 mg/L to *0.*12 mg/L when the temperature raised from *400 °C* to *600 °C* (pyrolyzed temperature in preparation of biochar) in the solution. Approximately *40-80%* of metal contained in wastewater was fixed into the sewage sludge. This justifies the high amount of certain metals in sludge. The concentration of metals in sludge depends on the origin of the sludge sample. Trace metals *(cobalt, copper and nickel)* concentrations were too low to be detected using the *XRF*.

3.5. Biochar yield

Pyrolysis process was performed and optimized at three different temperatures *(400, 500 and 600 °C)*, with a particle size of *100* and 250 μm at 10 min. Fig. 4 shows the biochar yield from the sludge in the pyrolysis process.

At *500 °C,* the yield for the 100 μm sample was *58%* while the one for 250 μm sample was *55%*. This was in agreement with what was reported by Agrafioti et al.*, (2013)* [12]. In this study, 10 min was sufficient for the pyrolysis reaction. The decrease in pyrolysis temperature increased the yield of biochar with high-quality adsorbent produced at an increased temperature of *600 °C*. The yield of biochar at *400 °C* reported as *82.8%* while the yield at *600 °C* was reported as *57.9%*. This could be possibly due to further conversion during pyrolysis, that is, a better primary decomposition of the sludge or the fact that the solid residue underwent a secondary decomposition [12]. A study by Agrafioti et al.*, (2013)* [12] observed a decrease of *32.5%* when the temperature was increased from *300 °C* to *500 °C*. Another study by Hossain et al.*, (2011)* [17], showed that the biochar produced through sewage sludge pyrolysis in a fixed bed reactor yield was *72.3%* of the same amount at *300 °C* and decreased to *52.4%* at *700 °C*.

3.6. Biochar surface area

The surface area of the biochar was determined as part of the characterization. It was observed that an increase in pyrolysis temperature

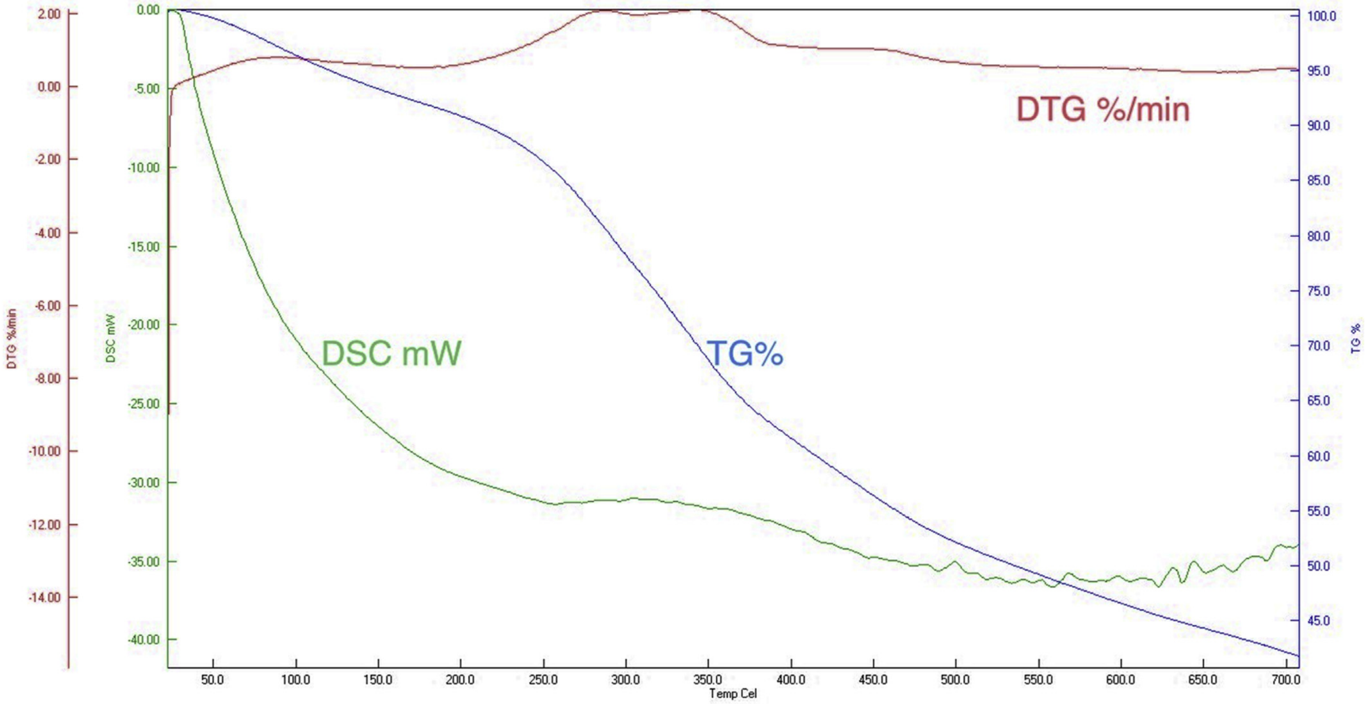

Fig. 1. Thermo degradation of sludge using thermogravimetric analysis.

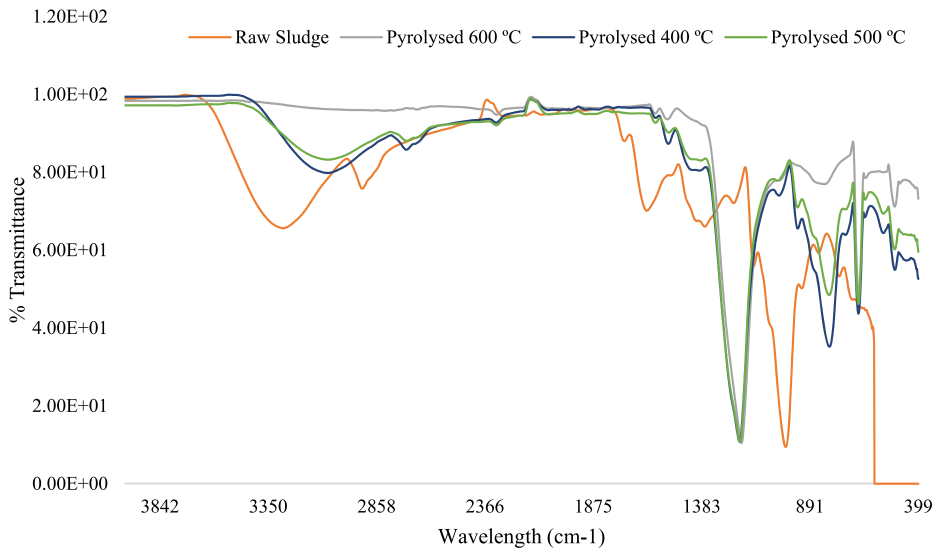

Fig. 2. FTIR spectra of raw sewage sludge and activated sewage sludge.

increased biochar surface area. The *BET* specific surface area was determined to be 355 m^2/g. There was an increase of about *30* m^2 *per gram* when the temperature was increased from *400* to *600* ^oC. This was in agreement with a study by Agrafioti et al*., (2013)* [12] that observed an increase of *13* m^2 when the temperature was increased from *300* to *500* ^oC. This was justified by the fact that there was a change in the structure of the initial feed *(sludge)*. The atomicity of biochar increased with an increase in pyrolysis temperature, hence the formation of micropores and mesopores which are linked to high surface areas. Besides the pyrolysis temperature and the characteristics of the feed, *BET* surface areas were affected by the process of production, the rate of heating and time of reaction [34,35]. According to Erto, A. et al.,. (2013) [36], *BET* area is not the key parameter for adsorption. High *BET* surface area was useful support to a great number of adsorption sites and increased capacity.

3.7. Surface morphology of raw sludge and biochar

The surface morphology of the raw sludge and the biochar at different temperature *(400, 500 and 600* ^oC) was analysed using scanning electron microscopy (*SEM)* and micrograph shown in SM Figure A2. It was observed that the surface morphology of the raw sludge showed pores on the surface of the residue, whereby the entire surface was covered by the white contaminates that could be inorganic and trace metals attached to the sludge as confirmed by SEM. The morphology of the surface at increased temperature *(400, 500 and 600* ^oC*)* showed an enhanced surface with space and structure (pores) because of temperature increase.

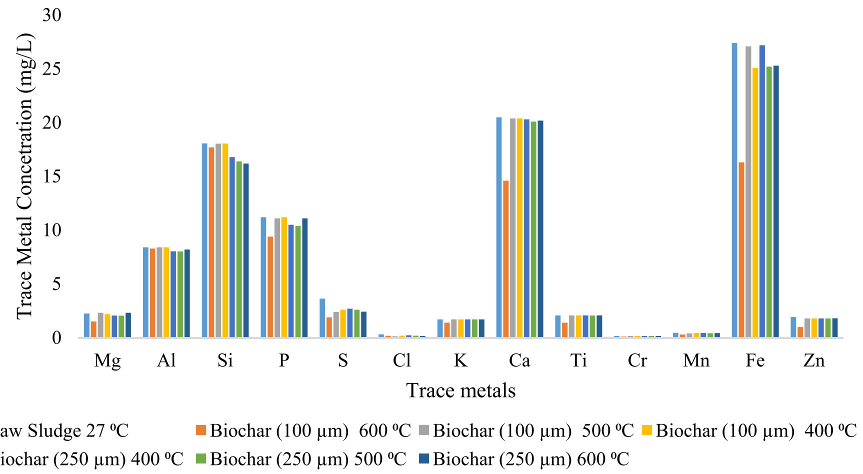

Fig. 3. Adsorption of trace metals solution under different pyrolyzed temperature and particles sizes of biochar.

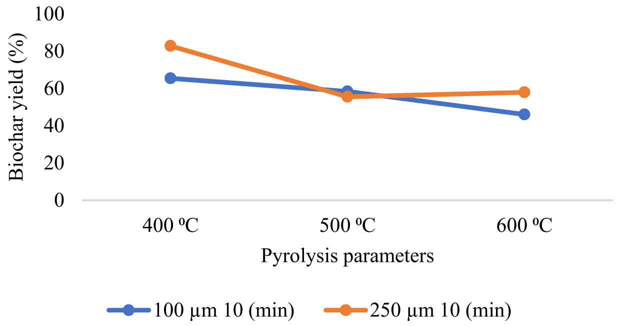

Fig. 4. Biochar yield from the sludge in the pyrolysis process.

The intervening space and structure promoted the adsorption of metal ions.

3.8. *Effect of temperature increase on the trace metal removal rate (adsorption)*

3.8.1. *Adsorption at 25 °C*

Trace metals *(Co, Ni and Cu)* removal rate *(RR%)* using adsorbent produced from sludge particle size *(*100 µm *and* 250 µm*)* and pyrolysis temperatures of *400 °C, 500 °C and 600 °C,* at the adsorption temperature of *25 °C*, in *10 hours* and 200 rpm was undertaken and the results presented in Fig. 5.

It can be observed that the highest rate of removal was achieved with the 100 µm biochar pyrolyzed at *400 °C, 500°C* and *600 °C* with the lowest registered at *600 °C* of biochar particle size of 250 µm. The efficiency of removal at *25 °C* of the three trace metals was high at *77.86% (600°C,* 100 µm*), 56.25% (600°C,* 100 µm*)* and *75% (600°C,* 100 µm*)* for the cobalt, nickel and copper respectively with low efficiency removal recorded at 59% *(400°C,* 250 µm*),* 40% *(600°C,* 250 µm*),* 59% *(400°C,* 250 µm*),* for cobalt, nickel and copper respectively. This indicated that the biochar produced had a strong affinity for trace metals *(copper, cobalt and nickel).* Cobalt and copper were compatible with the adsorption parameters, unlike nickel. The trace metal distribution reflects an interaction during the adsorption and adsorption capacity within the particles. Bio-sorbent showed a selective adsorption capacity towards the three metals ion (Ni, Co and Cu) A study by Hossain et al.*, (2011)* [17] reported that the effectiveness of the immobilization of trace metals by biochar was highly dependent on the type of contaminant found in the aqueous solution. A similar conclusion was drawn by Inyang et al.*, (2012)* [37], with an observation of high efficiency of removal for copper *(98%)* and low removal of nickel by *26%* that was attributed to the high sorption of

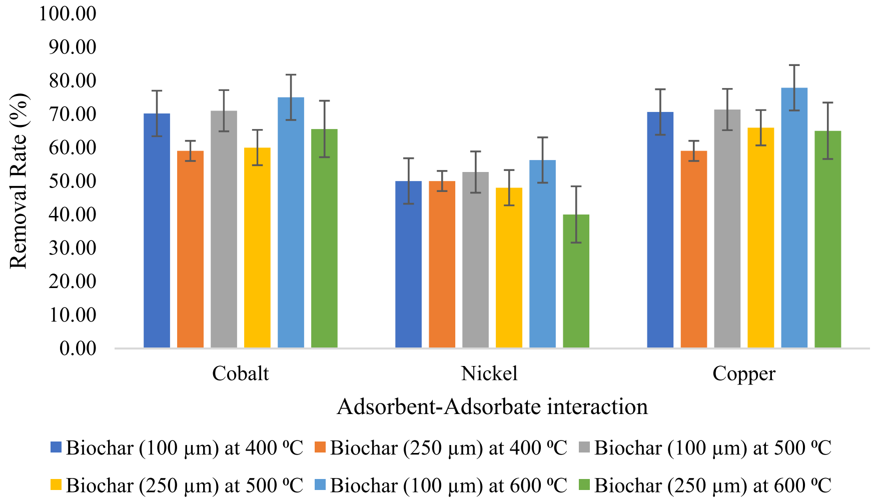

Fig. 5. Trace metal removal rate using sludge biochar particle size (100 µm and 250 µm) and temperature (400, °C, 500 °C and 600 °C) at agitation temperature of 25 °C in 10 hours.

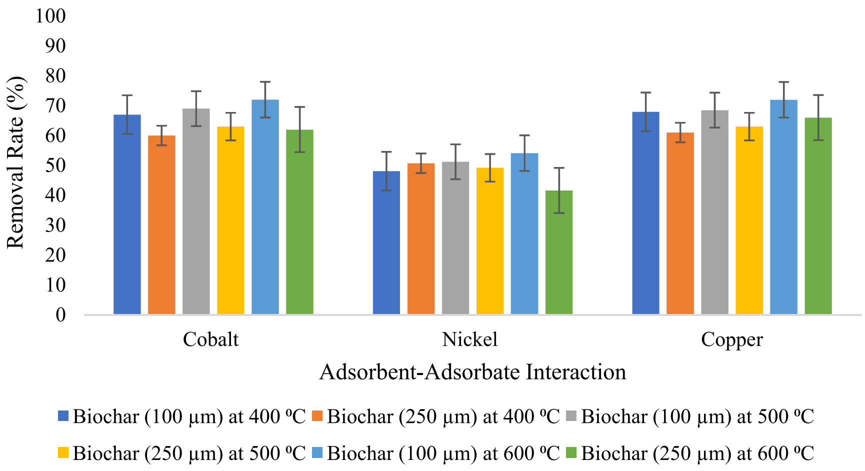

Fig. 6. Trace metal removal rate by optimization of the particle size (100 μm and 250 μm) and temperature (400, °C, 500 °C and 600 °C) at agitation temperature of 30 °C in 10 hours.

Table 1

Comparison of the Langmuir and Freundlich isotherm model constants and analysis errors of different metals by activated sludge adsorbent.

Parameters	Langmuir Isotherm Model			Freundlich Isotherm Model			
	q_r	b	R^2	1/n	n	k_f	R^2
Cobalt							
Pyrolyzed sludge at 400 °C	9.24	0.29	0.96	0.23529412	4.25	3.26	0.97
Pyrolyzed sludge at 500 °C	9.73	0.32	0.96	0.24096386	4.15	3.26	0.96
Pyrolyzed sludge at 600 °C	10.60	0.39	0.95	0.23809524	4.20	3.19	0.93
Nickel							
Pyrolyzed sludge at 400 °C	5.53	0.29	0.97	1.01010101	0.99	9.12	0.98
Pyrolyzed sludge at 500 °C	5.67	0.15	0.97	1.03092784	0.97	8.93	0.97
Pyrolyzed sludge at 600 °C	5.27	0.14	0.96	1.04166667	0.96	11.30	0.94
Copper							
Pyrolyzed sludge at 400 °C	9.40	0.50	0.97	0.53191489	1.88	5.60	0.95
Pyrolyzed sludge at 500 °C	10.13	0.34	0.97	0.48309179	2.07	5.22	0.98
Pyrolyzed sludge at 600 °C	11.08	0.44	0.94	0.40816327	2.45	5.46	0.97

certain trace metal from solutions due to their high constant of electronegativity. Inyang et al., *(2012)* [37] on the other hand, suggested that the electronegativity alone does not give a complete explanation to the rate removal.

3.8.2. *Adsorption at 30 °C*

Trace metals *(Co, Ni and Cu)* removal rate *(RR%)* using adsorbent produced from the sludge of particle size *(*100 μm *and* 250 μm*)* pyrolyzed at a temperature of *400 °C, 500 °C and 600 °C,* at the adsorption temperatures of *30 °C*, in *10 hours* and 200 rpm was undertaken and presented in Fig. 6.

Temperature was an important parameter for the adsorption process in the removal of the trace metals. It was observed that a small range of adsorption temperature *(25 °C and 30 °C)* did not have a significant effect on the rates of removal of trace metals concentration before and after the adsorption process. The high rate of pyrolysis temperature had a great effect on the adsorption process of the trace metals. Adsorption capacity increased with increase in adsorbent prepared from *400* to *600 °C* due to the diffusion of the molecules across the layers of the external boundaries, internal pores of the particles of the adsorbent that decreased the viscosity for the high concentration solution and change of the equilibrium capacity of the adsorbent. A decrease of adsorbent particle size from 250 μm to 100 μm and an increase in pyrolyzed biochar temperature from *(400, °C, 500 °C and 600 °C)* resulted in a high rate of removal of the trace metals from the aqueous solution. The efficiency of removal at *30 °C* of the three trace metals was high at *72% (600°C,* 100 μm*), 54.11% (600°C,* 100 μm*)* and *71.96% (600°C,* 100 μm*)* for the cobalt, nickel and copper respectively with low efficiency removal recorded at 60% *(500°C,* 250 μm*)*, 41.61% *(600°C,* 250 μm*)*, 63% *(500°C,* 250 μm*)*, for cobalt, nickel and copper respectively. The low-cost natural adsorbent (sludge) can be used as an adsorbent due to its capacity of the metal binding.

3.9. *Adsorption isotherm modelling*

Adsorption isotherm was studied using Langmuir and Freundlich isotherm models at equilibrium. Langmuir isotherm model was used to predict the mono-layer adsorption surface of the active site. This involved the interaction between the trace metal ions and the absorbent by utilizing excel data fitting to the linear Langmuir model. It assumed that there no interaction among the adsorbed molecules on the adsorption sites neighbouring. Langmuir parameters; q_r *(adsorption capacity of the maximum mono-layer)* and *b (Langmuir constant that was related to the energy of adsorption*) and coefficient of determination *(*R^2*)*.

Freundlich isotherm model was used to describe the multi-layer physio-chemical adsorption on the heterogeneous surface. It assumed that binding sites were occupied first and adsorption strength decreased with the occupation degree. Freundlich parameters*;* K_f *(Freundlich constant that represented the adsorption capacity and adsorptive bond*), n (heterogeneity factor that represented the relative distribution and adsorption intensity of the energy) and coefficient of determination *(*R^2*)* were determined. Table 1 shows the comparison of the Langmuir and Freundlich isotherm model parameters and analysis errors of metals *(Co, Ni and Cu)* by activated sludge adsorbent at *400 °C*, *500 °C* and *600 °C*.

Freundlich and Langmuir isotherm model described the distribution of adsorption energy into the adsorbent heterogeneous surface. Adsorbent at high concentration was well described by the Langmuir isotherm while Freundlich isotherm model described the adsorbent at low concentration. Adsorption was directly proportional to the surface fraction of the adsorbent as described by Langmuir model [27,38,39]. Isotherm model with equilibrium data was well represented by the Freundlich model with a high coefficient of the correlation that defined the distribution exponential of active sites and surface heterogeneity. According to the Bhandari V.M. et al., (2014) [8], and Sahoo, S. et al. (2013) [38], 1/n that is a function of the adsorbent strength indicates affinity between the adsorbate and adsorbent. The value of $1/n < 1$ implies that the adsorption process is a chemical process, $1/n > 1$ implies that the adsorption process is a physical process, $1/n$ approaches zero when the surface was heterogeneous. The adsorption process of the cobalt and copper was a chemical process and that one for nickel was a physio-chemical process. The value of $n > 1$ as showed in cobalt and copper indicated a favourable adsorption process. The value of n and K_f increased with an increase of the adsorbent pyrolyzed temperature in the removal of the trace metals. The variation of K_f indicated that the adsorption energies *(bonding energy of the adsorption reaction)* between the metal ions *(adsorbate)* and adsorbent were different. High K_f that is correlated with fast adsorption was observed in the physio-chemical process of the nickel removal. The q_r indicated limiting adsorption capacity when the adsorbent surface was fully covered metal ions *(adsorption capacity of the maximum mono-layer)* [28]. The correlation coefficient (R^2) of both Langmuir and Freundlich isotherm models ranged from *0.93* to *0.98*. This was an indication of the fewer errors in the experiment. The adsorption capacity of the metal ions using the sludge as adsorbent was within the range of the natural materials described by Wand, B. et al. (2017) [7] and Geçgel, Ü. et al. (2012) [26].

3.10. Cost-effectiveness of the sludge as an adsorbent

Cost-effectiveness of the adsorbent is important to the process and varies with feedstock availability and the employed technology processes. The organic adsorbent needs extra heat and chemicals to activate to carbon. This adds extra cost *(electricity, maintenance, labour, chemical and transportation)* to the process required thermodynamic *(mass and energy balance)* principles, logistics modelling, maintenance and operation cost, chemical costs that were not applied in the research. The improved low-cost adsorbent compensates these costs and is economically attractive for the metal uptake as it minimized the treatment cost and enhanced metal removal performance. Other techniques for the removal of trace metals from aqueous solution are: reverse osmosis, oxidation, precipitation, ions exchange and filtration have been reported to be expensive and inefficient in cases where the water contains trace metals in trace amounts [6,21]. Activated carbon is the most used adsorbent in the adsorption process. Due to the fact that the use of activated carbon is readily available and inexpensive [6,22]. Less expensive alternatives such as sludge become an economically viable technology. The other advantage of biochar from sludge, as an adsorbent, is that the process was done at relatively low cost and was an environmentally friendly process for wastewater treatment [6,18]. The biochar can act as an innovative adsorbent for the treatment of wastewater by utilization of the activated sludge.

4. Conclusions and recommendations

The study showed that biochar produced from sludge can effectively remove trace metals from aqueous solutions. The effectiveness of the sorption was affected by the biochar pyrolysis temperature, agitation temperature and nature of the mineral components from the biochar. Adsorption was directly proportional to the surface fraction of the adsorbent. The adsorption capacity of the metal ions using the sludge as adsorbent was within the range of the natural materials. Hence, biochar produced from sludge can be an alternative adsorbent for commercial activated carbon or other materials for the removal of trace metal in wastewater treatment processes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cscee.2020.100018.

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