Original Research Article

Composite material of clay-biochar for cadmium ion removal from water

Abstract

A research study of the synthesis of nanocomposite of clay-biochar material acquired from normal clay and biomaterial of *Prosopis Juliflora* for cadmium ion removal from aqueous solutions is reported. Composite materials were prepared by heating of ordinary clay and biomaterial of *Prosopis* at 500 °C temperature and the synthesis was established with XRF, EDX, FTIR, XRD and SEM characterization. The results of characterized material showed that clay minerals successfully permeated the surface of biochar materials to form composites. The effectiveness of the composites in removing cadmium metal was determined by a batch adsorption procedure. The composite material produced a removal efficiency of 99% of cadmium ions. Adsorption was investigated using the adsorption isotherms of Freundlich and Langmuir which showed correlation r^2 values of 0.924 and 0.932 respectively for the removal of cadmium ions from water. The results also revealed a pseudo second-order reaction for cadmium ions removal

Key words**: *Clay-biochar, composite material, cadmium, adsorption***

Introduction

Water as a commodity is essential for humans and other living organisms. Clean drinking water is a basic requirement for good health. On 28 July 2010, the United Nations General Assembly documented the rights of animals to water and sanitation through resolution 64/292. The resolution recognizes that clean drinking water is essential for the realization of human rights and calls on states and international organizations to provide clean, affordable and accessible drinking water and sanitation for all [1]. However, in certain environments, anthropogenic activities associated with mining and various industrial uses can naturally exceed guidelines for water quality and safe drinking water [2]. Heavy metals such as Cr, Cu, Ni, Zn, Pb, Cd, and Hg, are a major concern because of their toxicity and persistence in the environment [3]. Heavy metal contamination of water poses particular risks to humans and animals due to bioaccumulation in food chain [4]. Inhalation of high levels and prolonged interactive contact with cadmium oxide vapours can lead to acute pneumonia with pulmonary edema, which in severe cases can be fatal [5]. The main target organs in the body where this metal is toxic are the lungs, kidneys and bones [6]. The maximum permissible level of cadmium in drinking water is 0.005 mg/L according to USEPA, EU and KEBS and 0.01 mg/L according to NEMA standards.

Environmental pollution of water is a major threat, and researchers are interested in developing inexpensive and effective techniques for the removal of heavy metals from various environmental matrices. The use of nanotechnology and nanocomposites in the treatment of waste water has gained traction of researchers with advances in fiber, metal nanoparticles, nanophotocatalyst, nano membranes and heterojunction nanomaterials as the latest trends [7]. The use of clay as adsorbent is novel since it is available natural and at a low cost [8]. Many studies have shown that biochar is important in improving soil properties and increasing crop yields [9,10,11]. Biochar and its activated derivatives remove various contaminants, including pathogens [12– 15], inorganic substances such as heavy metals [16, 17], and organic impurities such as dyes [18,19], due to their improved properties such as high carbon content, larger surface area, high cation/anion exchange capacity, and stable structure [20]. The use of biochar and its modification using acid oxidation increases the functional groups of biochar cation exchange capacity, micropores, specific surface area and oxygen content [21]. The use of biochar as a safe, potential low-cost and sustainable technology for treatment of wastewater has been reported, although its technological use has been constrained by lack of design information and environmental public health risk constrains. Largely untapped opportunity is to convert agricultural wastes (such as crop residues) from system of production into biochar by pyrolysis and its use for water treatment [22]. However, the use of biochar from *Prosopis Juliflora* has not been exhausted to remove contaminants especially heavy metals. *Prosopis Juliflora* plant is an invasive plant that has taken over rangelands in arid and semi-arid which is becoming a menace to both farmers and pastoralist in the world. Proper use and management of the *Prosopis* will be a blessing to those affected by its spread [23]. Specially in the arid and semi-arid region of Kenya. In this study clay-biochar nanocomposite materials were synthesized and tested for their adsorption of cadmium ions in aqueous media. The novelty is in the use of locally available clay and biochar from invasive species of *Prosopis* that will help in the containment of its spread for proper management and use.

Materials and methods

Study area and Sampling

The ordinary clay was picked up from the Kimathi Valley, Mukurweini sub-county, Nyeri county (0°37'55.9" S, 37°9'43.8" E). Sampling of *Prosopis Juliflora* was carried out on the edges of Tana River in Garissa county (0° 27' 50" S, 39° 38' 12' 'E). Figure 1 and Figure 2 shows the study research areas from where sample materials were collected.

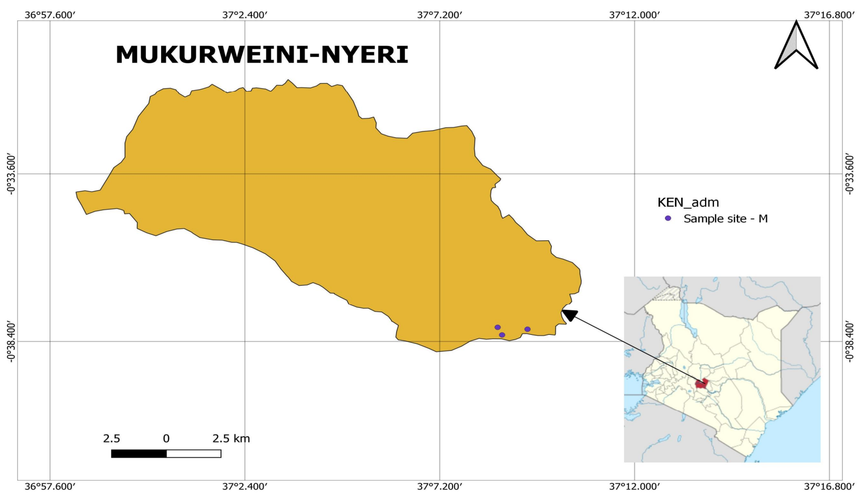

Figure 1: Sampling area in Mukurweini, Nyeri County

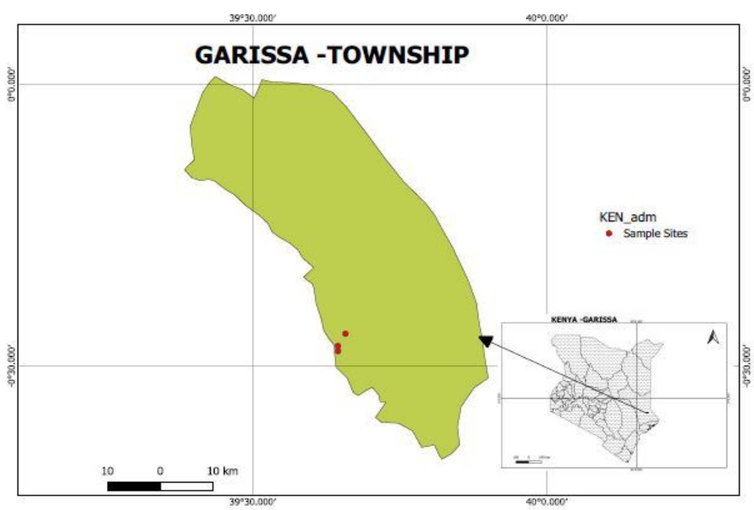

Figure 2: Sampling area in Garissa Township, Garissa County

Experimental procedure

The collected clay was pre-treated to eliminate impurities. The fresh clay was washed with a sufficient amount of deionized water, stored for 24 hours, decanted until the decanted water was completely clear, and then air dried. The dried clay was then ground and sieved. Calcination of the clay was performed at 1000°C for 1 hour using a furnace (Daihan FHX, Digital Muffle Furnace, Standard Type, 1200°C, FHX-03/05/12/14/27/63). The small portions of *Prosopis* were dried, ground and the ground powder were dried in the air 24 hrs to decrease the amount of moisture. The pyrolysis of *Prosopis* and calcined clay to form composite was performed using the same furnace at 500 °C. In general, as the temperature of biochar production increases, so does the pH value of the resulting biochar. Oxygen-containing acidic functional groups that contribute to the acidity of biochar at low temperatures loses oxygen at high temperatures, increasing the pH of biochar as the pyrolysis temperature increases [24]. The calcined clay and biomaterial were pyrolyzed in a 1:1 ratio.to form the composite material at 500 ^{o}C temperature for 2 hours. At the start, the same amount of calcined clay and biochar was used in each case, then different ratios were used to achieve the optimum dispersion for impregnation. However, researchers report that for equal dispersion of the two materials to be achieved the equal amount is the recommended dosage for mixing of the two materials [25]. After the pyrolysis process, the oven was left for a while to cool to room temperature. Nanocomposite materials were characterized with Fourier-transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM) (JEM-2100F), Scanning electron microscopy (SEM) (model; Quarto S), XRF, EDX, and X-ray Powder Diffraction (XRD) (Rigaku powder XRD model Ultima IV, conditions: start angle 5, stop angle 70, scan speed 5). Analysis of the nanocomposite materials elemental composition was performed using X-ray fluorescence (XRF) and Energy Dispersive X-Ray Analysis (EDX). XRD of the composite was done to decide the phase analysis. Morphological studies and size measurement were performed by FESEM and TEM. In the FTIR investigation, pellets were prepared using potassium bromide (KBr). A batch adsorption technique was used to examine the efficiency of cadmium removal by nanocomposite material. Mixed standards of heavy metals that contains cadmium (1000 mg/L) was put in a 1-liter flask to accomplish a 1 mg/L concentration of cadmium ion. A 25 mL of cadmium ion diluted solution was placed in a flask and the suitable dose (1,2 4 6 mg) of nanocomposite was added while keeping the rest of the parameters constant (contact time, agitation speed, and pH) i.e. 120 min, 150 rpm, and pH-8 respectively. pH adjustments were made with HCl or NaOH (dilute) to reach the required pH. Removal efficiency was achieved using Equation 1 established on the reduced concentration of cadmium for each sample.

$$\% \text{ efficiency of removal} = \frac{(C_i - C_f) \times 100}{C_i} \qquad \text{---------------------------------} \quad (1)$$

Where C_i is the original metal ion (mg/L) concentration and C_f is the metal ion equilibrium concentration after the adsorption process (mg/L).

Results and Discussion

Elemental analysis by EDX indicated that the composition of the nanocomposites was rich in C, O, Si, Al, and Fe. Carbon originated from biochar while the other elements emanated from clay. The content was 49.05 % C, 35.85 % O, 5.7 % Si, 5.2 % Al and 2.05 % Fe as shown in Figure 3 (A) and (B).

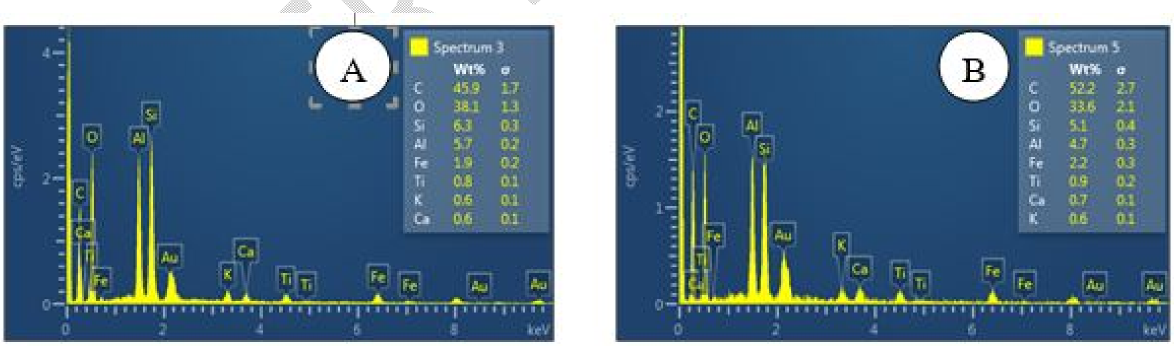

Figure 3: Patterns/Images of composite material duplicate (A) and (B) using EDX (pH=8, shaker speed=150 rpm, Contact time=120 min, Cd conc= 1ppm)

The FTIR spectrum of the nanocomposite material presented a broad peak at around 3645 cm^{-1} and 2349 cm^{-1}, which is symbolic of O-H stretching and CO_2 absorption respectively. The peak at 1063 cm^{-1} was assigned to the vibration of C-O stretching. Therefore, it indicated that the material of the biochar content was contained well in the nanocomposite, indicating the effective clay content impregnation onto the biochar surface as shown in Figure 4.

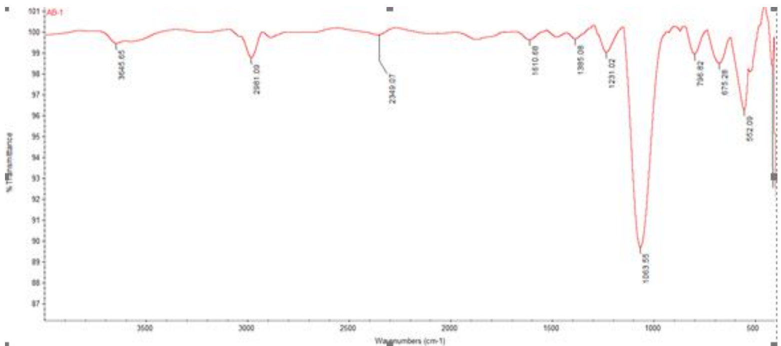

Figure 4: FTIR spectrum of nanocomposite material (pH=8, shaker speed=150 rpm, Contact time=120 min, Cd conc= 1ppm)

XRD of the nanocomposite revealed the presence of mineral crystals, as shown in Figure 5. In the image, three (3) peaks appearing at 19.9^0, 25^0 and 35^0 were recognised as expandable phyllosilicates [26]. These XRD results were in good agreement with the results of EDX, indicating that the process of pyrolysis effectively impregnated clay minerals onto the surface of the biochar to produce clay-biochar composite material.

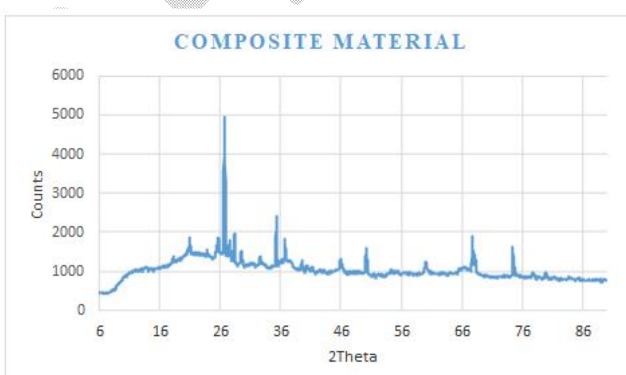

Figure 5: XRD pattern of clay-biochar nanocomposite (pH=8, shaker speed=150 rpm, Contact time=120 min, Cd conc= 1ppm)

Figure 6 and Figure 7 shows images of SEM of the clay-biochar composite. They indicated that the surface of the sample was largely covered with a thin film structure exhibiting a layered surface, and also exhibited a distinct morphology typical of clay, indicating an impregnation success of content of the clay minerals on the biochar surface as confirmed by EDX analysis as showed in Figure 8.

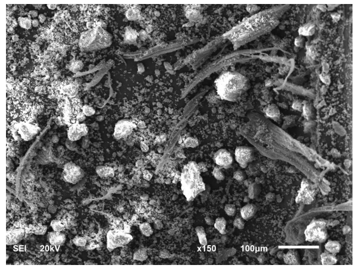

Figure 6.: SEM images of nanocomposite at 100 µm (pH=8, shaker speed=150 rpm, Contact time=120 min, Cd conc= 1ppm)

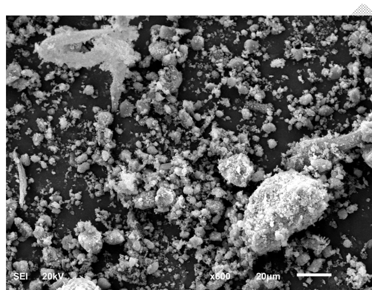

Figure 7: SEM images of nanocomposite X5 at 20 µm(pH=8, shaker speed=150 rpm, Contact time=120 min, Cd conc= 1ppm)

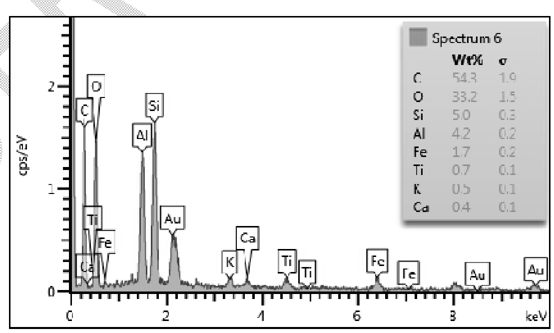

Figure 8: EDX spectrum of the nanocomposite (pH=8, shaker speed=150 rpm, Contact time=120 min, Cd conc= 1ppm)

The following parameters were considered for the batch sorption analysis; pH, contact time, shaker speed, material dosage, and optimization of each of them [27]. The removal efficiency of the nanocomposite material for cadmium ions from water was 99.5% as shown in Figure 9. For the Freundlich isotherm sorption data, the r^2 fit for the composite was 0.924 and the r^2 fit for the Langmuir isotherm sorbent composite was 0.932, as shown in Figures 10 and 11, respectively. Experiments of Kinetics indicated that the second order model close-fitting the data better than the first order model, as shown in Figure 12. The second-order model showed a linear fit, but the pseudo first-order model did not.

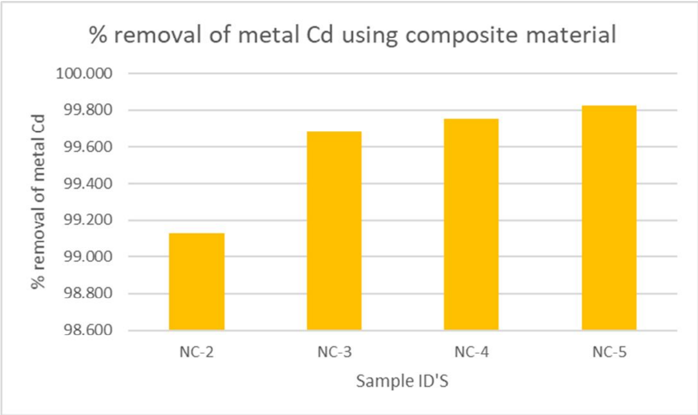

Figure 9: Removal efficacy of composite material of Cd ions (pH=8, shaker speed=150 rpm, Contact time=120 min, Cd conc = 1ppm)

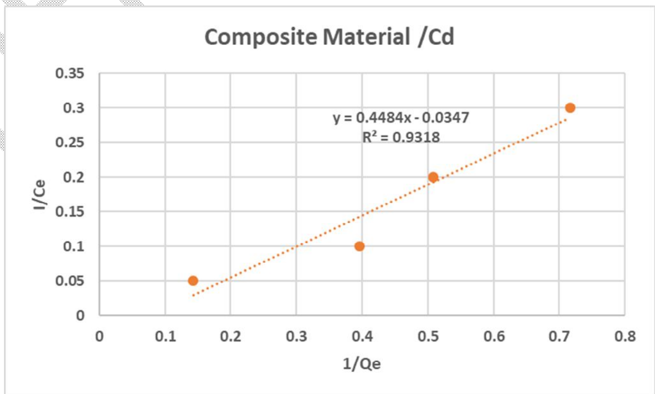

Figure 10: Freundlich isotherms for composite meterial demonstrating trends in cadmium ion adsorption (pH=8, shaker speed=150 rpm, Contact time=120 min, Cd conc= 1ppm)

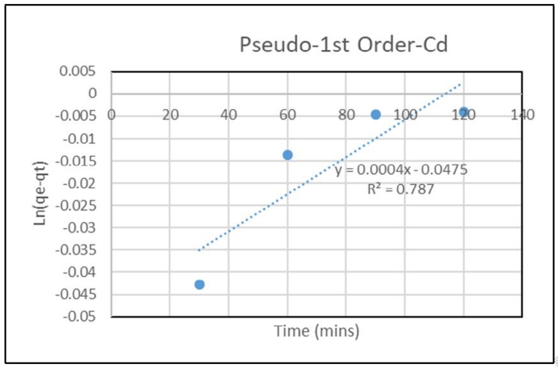

Figure 11: Langmuir isotherm for composite material demonstrating trends in cadmium ion adsorption (pH=8, shaker speed=150 rpm, Contact time=120 min, Cd conc= 1ppm)

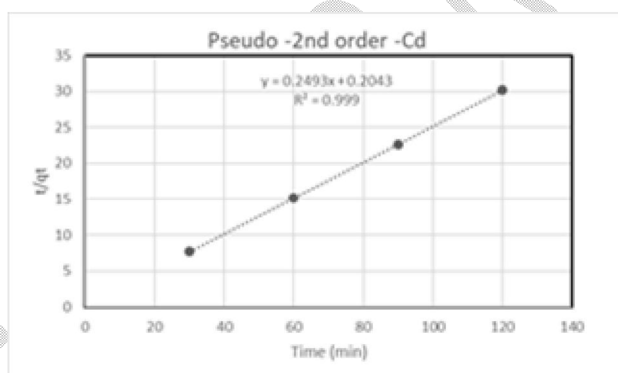

Figure 12: Plot of Pseudo First and second order models of cadmium ion (pH=8, shaker speed=150 rpm, Contact time=120 min, Cd conc= 1ppm)

Conclusion,

This research study focused on the synthesis of a clay biomaterial composite of *Prosopis* for the removal of cadmium ions from water. The composites were developed by calcining the clay and biomaterials at a temperature of 500 °C, and the synthesis of the nanocomposites was determined by XRF, EDX, FTIR, XRD and SEM characterization techniques. Analysis of the characterized material showed that the surface of the biochar was impregnated with clay mineral crystals to produce a composite material. A batch adsorption process was used to study the removal efficiency of cadmium ions by the composite. The composite material has shown remarkable efficiency in removing cadmium ions from water. Freundlich and Langmuir isotherms were used to study the adsorption of cadmium ions. Both showed good suitability for removing cadmium ions. The results also established a pseudo-model for secondary reactions to remove cadmium ions.

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