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**LOCAL ACTION WITH INTERNATIONAL COOPERATION TO IMPROVE AND
SUSTAIN WATER, SANITATION AND HYGIENE SERVICES**

**Low-cost biomass as adsorbents for the removal of
heavy metal from industrial wastewater used for
crop irrigation in developing countries**

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Freshwater scarcity has prompted farmers in developing countries to rely on wastewater for agriculture. However, the concentrations of heavy metals in the wastewaters are found to be above the WHO/FAO recommended thresholds. This inherently presents concern particularly as it relates human health. Although, several conventional wastewater treatment technologies exist; their applications are limited by high procurement, operation and maintenance costs. Currently, studies on biomass wastes as low cost adsorbents are gaining momentum. In this study, coco-peat was considered for heavy metals removal. In this context, batch experiments were carried out in triplicates at 3 different contact times and pH. After 2hr of contact time at pH9, the coco-peat was proven to have Cr removal efficiency of 91.6% against 73.2% using an activated bone char; and 95.0% for Pb(II) against 91.2% for the bone char. This suggests that the use of coco-peat can provide cost effective means for metal removal from industrial wastewaters.

Introduction

The scarcity of freshwater resources being currently experienced in water stressed and most developing countries has prompted millions of smaller communities to depend on wastewater for agriculture, drinking, bathing and fishing. In this context, the treatment option of metal-bearing wastewater as it relates to agriculture will be considered. The economic contributions of farmers in developing countries are now severely restricted by the scarcity of water resources which is observed to affect the expansion of agricultural yields and quality of crops. Although, numerous benefits of wastewater reuse in agriculture have been widely reported from around the world; it is particularly most beneficial and cost-effective in developing countries (Drechsel, *et al.*, 2009). However, the major constraint to this agricultural practice is poor management of the resource, lack of efficient and affordable treatment facilities.

In developing countries, industries producing textile and tannery products are among the major employers of labour and are known in contributing to the nations' GDP per capita income. However, despite these huge opportunities and economic benefits, it is apparent that such industries among others do only partial treatment of their wastewaters or in most cases do not treat before discharging the effluents into nearby waterbodies (Becerra-Castro, *et al.*, 2015). Regrettably, farmers along the fringes of these waterbodies use them predominantly for crop irrigation. Textile and tannery wastewater contain contaminants such as heavy metals, dyes, starch, salts and micro-organisms. Prolong exposure to these kinds of pollutants can lead to pervasive consequences on crops and human through food chain. There are well documented reports that establish epidemiological links between consumption of ill-irrigated food crops with individual or societal illnesses (Blumenthal & Peasey, 2002).

There are several publications from some of the development countries where concentrations of different heavy metals in food crops irrigated by industrial wastewater exceed the WHO/FAO recommended thresholds. Among the countries where textile and tannery wastewaters are used for crop irrigation include

Nigeria (Akan, et al., 2009), Bangladesh (Islam, et al., 2013), India (Chhikara and Rana, 2013), Pakistan (Khan et al., 2013). The international guidelines jointly issued by World Health Organization (WHO) and Food and Agriculture Organization (FAO) were essentially to limit the concentration of wastewater contaminants in irrigation water, agricultural soils and plants in order to protect humans and animals health (FAO/WHO, 2006). However, while the application of these guidelines have been successful in the developed countries; their effective implementation in developing countries have not been successful (Ensink and Van Der Hoek, 2009). The reasons for this unsuccessful implementation may be due to: 1) high cost of procuring and installing modern wastewater treatment facilities; 2) poor legislation on enforcement of the guidelines; 3) poor monitoring and evaluation strategy. However, in this scenario the focus of this study is anchored to the first reason, which has prompted the search for a simple and affordable technique to treat industrial (textile and tannery) wastewater, so that the 'cleaned water' can then be applied for irrigation purposes.

Over the years, wastewater treatment technologies that have emerged include chemical precipitation, ion-exchange, electro dialysis, reverse osmosis/membrane, and adsorption using commercial activated carbon and other non-easily accessible industrial by-products (Geetha and Belagali 2013). Of all the treatment methods mentioned above, only activated carbon is effective in removing wastewater pollutants such as heavy metal ions even at much lower concentrations. Another limitation of the conventional treatment methods other than the use of activated carbon is the production of secondary toxic wastes which may require additional cost of treatment. Wastes generated from these methods are mostly non-ecosystem friendly. Against this backdrop, recent studies have shown that the use of cheaper environmental friendly biomass wastes as adsorbents for the removal of contaminants from wastewater are gaining momentum (Geetha & Belagali, 2013; Saka et al., 2012; Vlaev et al., 2011).

Application of this research to improve the quality of wastewater used for agriculture

Studies into the application of plant or animal biomass wastes as adsorbents for the removal of contaminants from wastewater are still in their developing phase. This study sought to investigate the adsorption potential of coconut peat (or coco-peat) for removal of heavy metals, and comparing its sorption efficiency to that of commercial activated bone char. In this case, the heavy metal ions of interest include Cr^{+6} , Cu^{+2} , Fe^{+2} , and Pb^{+2} present in textile and tannery wastewater. In other to investigate the optimum operating conditions for adsorption of the heavy metal ions by coco-peat, three batch tests with their corresponding controls were conducted. The operating conditions considered for the adsorption include pH, contact time, temperature and adsorbent dosage. While the adsorbent dosage of 1.5g and temperature of 25 ± 2 °C were kept constant, pH values (11, 9 and natural/acidic) and contact time (2-hr, 4-hr, and 6-hr) were varied.

Materials and methods

Materials and preparation

Reagents

All reagents used in this study were of analytical grade, supplied by Fisher Scientific Equipment Laboratories Ltd., Loughborough, United Kingdom. A standard ICP solution was prepared in nitric acid with concentration of 10,000 mg/L for CuSO_4 and $\text{Pb}(\text{NO}_3)_2$, and 1000 mg/L for K_2CrO_4 and FeSO_4 . Approximately 0.5 ml of $\text{Pb}(\text{NO}_3)_2$ and CuSO_4 were withdrawn and poured into a separate 1000 ml (1 L) volumetric flask, and then 5.0 ml of K_2CrO_4 and FeSO_4 were carefully measured and added into the flask. To prepare the required 5 mg/L of the standard solution needed for the adsorption studies, Purite water was added to the flask to make 1 litre. The procedure for the wastewater preparation was based on the method outlined in Standard Methods for the Examination of Water and Wastewater (APHA, 2012). The wastewater was formulated to contain the heavy metals (Cr^{+6} , Cu^{+2} , Fe^{+2} , and Pb^{+2}). The pHs of the wastewater were adjusted to 9 and 11 (alkaline) which are typical of textile and tannery wastewater by the addition of few drops of NaOH. While controlled tests were carried out in just purite water without any pH adjustment.

Adsorbent

Fig. 1 (a) depicts a loose and highly fibrous spongy-like fibre of coconut, Fig. 1 (b) is a compressed dried coco-peat (coir) processed and supplied by Fertile Fibre, Withington, Hereford, United Kingdom. The compressed coir was then shredded as shown in Fig. 1 (c). The shredded coir was then ground in a blender

and sieved to a desired particle size of 600-850 μm using British Standard (B.S.) mesh sieves. The raw coco-peat was washed thoroughly with clean tap water to remove all dirt and dust, and further rinsed with Purite water. The coir was spread on clean plastic tray and placed in an air-oven incubator operated at 40 $^{\circ}\text{C}$ for 24 hours. Commercial activated bone char was used as a benchmark to compare its adsorption efficiency to that of the model adsorbent (raw coco-peat). The activated bone char was supplied by Jeret Limited, 4 Birchgrove, Houston, Johnstone, Renfrewshire, Scotland. The bone char was then reduced to the required granular particle size of 600-850 μm before being washed with cleaned water and rinsed with purite water before the adsorbent was dried in an oven for 12 hours at 105 $^{\circ}\text{C}$. No form of treatment was carried out on both adsorbents before being stored in an airtight plastic container and kept in a cold room at 4 $^{\circ}\text{C}$ for future use. Fig. 1 (d) is the granular activated bone char.

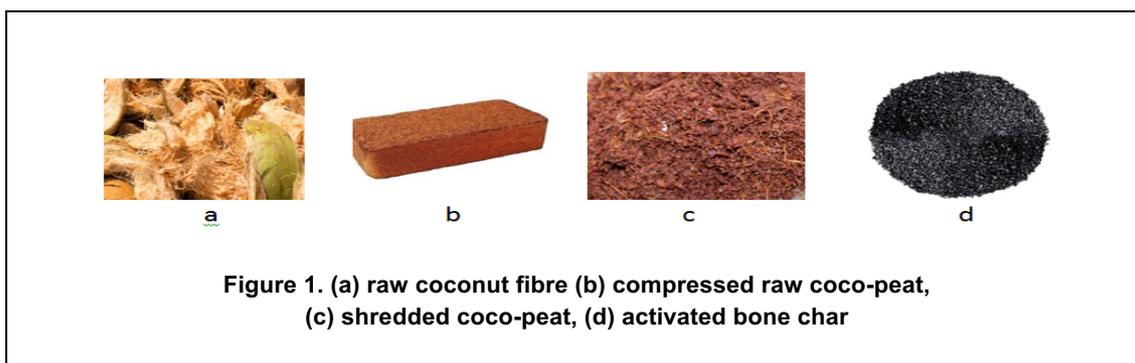


Figure 1. (a) raw coconut fibre (b) compressed raw coco-peat, (c) shredded coco-peat, (d) activated bone char

Determination of surface area using BET technique

The precise specific surface area, pore size and pore volume of the coco-peat and activated bone char were measured as a function of relative pressure using automated BET (Brunauer–Emmett–Teller) analyser (Micrometrics, TriStar 3000, Micromeritics Instrument Corporation, Norcross, GA, USA). To carry out the tests, the sample handler was weighed without and with adsorbent samples, which occupied an area of about 10–20 square metres. This was followed by placing the adsorbate in a heating mantle for degassing and dewatering which took about 1-2 hours at very high temperature set at 200 $^{\circ}\text{C}$.

SEM/EDS analysis

Characterisation of the coco-peat and the activated bone char were carried out using scanning electron microscopy (SEM), energy dispersive spectrometry (EDS). The surface morphology of the adsorbents were examined using SEM at different magnifications (100x, 250x, 1000x and 5000x). The magnification that produce clearer image is then selected for interpretation. The EDS on the other hand, was employed to quantify the elemental composition in the adsorbents.

Batch adsorption and pH adjustment

The experiments were conducted in three batches with each carried out in triplicates, which correspond to the selected pH (9, 11, and natural). Furthermore, three separate control tests were ran (adsorbents mixed with just purite water) according to the chosen pH value. For each batch test, a fixed amount of 1.5 g adsorbent was weighed and placed in separate conical flask, and 50 ml of the standard aqueous solution with concentration strength of 5 mg/L was added. The mixture was then stirred using a magnetic stirrer attached to Mettler Delta 340 pH Meter to measure the respective pH values before and after adsorption based on the given contact time (2-hr, 4-hr, and 6-hr). All conical flasks were then placed in a mechanical shaker (Adjustable GALLENKAMP Orbital Incubator-cooled Shaker) which was pre-set to a temperature of 25 ± 2 $^{\circ}\text{C}$ and a speed of 150 rpm. Each sample was removed from the shaker at the end of each contact time and was filtered using a Whatman paper No. 42 to separate the filtrate from the solids. The concentrations of Cr, Cu, Fe and Pb in the wastewater following adsorption were analysed using Inductively Couple Plasma Atomic Spectrometry (ICP-AES-9000, Shimadzu Scientific Instruments, Japan).

Heavy metal removal efficiency

To determine the percentage adsorption of metal ions by the adsorbents, the following equation as described by (Chen and Wang, 2008) was used:

$$R\% = \left[\frac{C_i - C_f}{C_i} \right] \times 100$$

where C_i is the initial of metal ions concentration in the synthetic wastewater (mg/L), C_f is final metal ions concentration in each filtrate – after adsorption (mg/L).

Results and discussion

SEM/EDS

Fig. 2 (a and b) shows SEM images of coco-peat magnified at 250x and 1000x respectively. The coco-peat (coir), was A careful study of these images is expected to further enhance the understanding of the surface characteristics of the materials. Fig. 2(a) at magnification of 250x presents a roughage and ridge-like features with a major crevice across the section, indicating active sites for metal binding. Fig. 2(b) (at a magnification of 1000x) appears to have smooth exterior surfaces and non-visible pores, yet uneven, which denotes that the particles are naturally held together by cohesion. The smooth surface may be as a result of melting and fusion processes of lignin and other small molecules in the coco-peat such as pectin and inorganic compounds. It is also an indication of the presence of lignin and cellulous. Fig. 2(c) shows large grain crystallizations of bone char at magnification of 250x whereas Fig. 2(d) shows small grains merge crevices next to each other at magnification of 1000x. Both Figs. 2(c and d) looks sturdy but appear more porous with a good number of active sites for metal binding.

Results from the EDS analysis shows that elemental compositions in coco peat comprise 54.0% C (carbon), 42.7% O (oxygen), 0.2% Ca (calcium), 1.4% K (potassium), 0.4% Na (sodium), 0.2% Si (silicon) and <1% of other elements. In the case of activated bone char, the elemental composition consist of 20.0% C; 35.0% O, 28.6% Ca, and 12.3% P (phosphorus), 1.8% Pd (palladium), 0.5% Na, 0.5% Mg (magnesium), 0.5% Al (aluminium), 0.4% Si (silicon) and 0.4% Fe (iron).

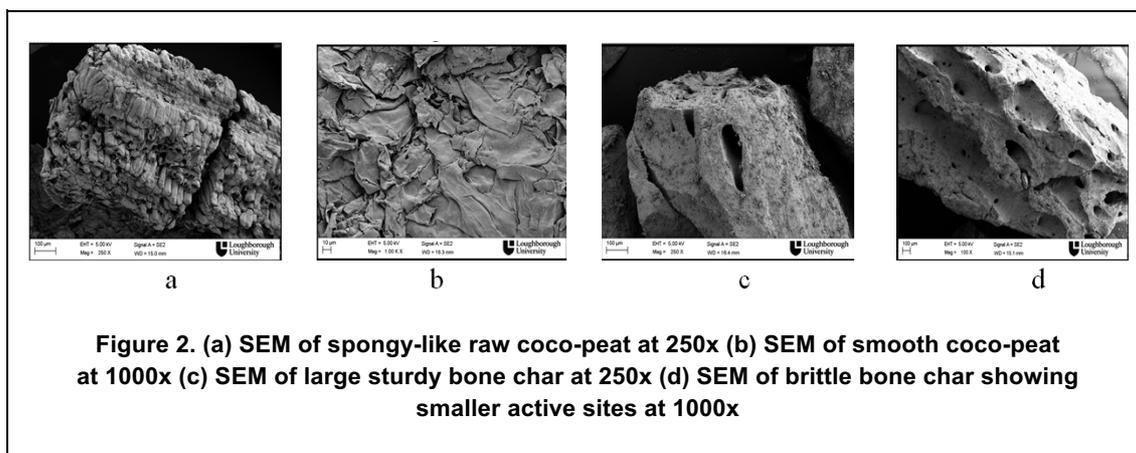


Figure 2. (a) SEM of spongy-like raw coco-peat at 250x (b) SEM of smooth coco-peat at 1000x (c) SEM of large sturdy bone char at 250x (d) SEM of brittle bone char showing smaller active sites at 1000x

Fourier Transform Infrared Ray (FTIR) analysis of coco-peat

The FTIR analysis of coco-peat reveals strong absorptions as shown in Fig. 3. The characteristics bands of the functional groups in the cellulose structure were observed at 3324.27 cm^{-1} (hydroxyl stretching vibration), 2917.46 cm^{-1} (methylene stretching vibration), and 1030.19 cm^{-1} (1,4-glycosidic band). Besides, the wave number at 1605.59 cm^{-1} was ascribed to the skeletal C=C stretching vibration in the aromatic rings bands of lignin. Also, appearance of an absorption band at 1420.68 cm^{-1} was related to the stretching vibration of C–O–C group ring vibrations of carbohydrates. The strong band at 1368.41 cm^{-1} is characteristic of weak vibration of the aliphatic N–O group. The stretched adsorption peak at 529.57 cm^{-1} could be assigned to the presence of alkyl halide (C–X) and disulphide groups. The existence of C–O of carboxylic acid groups gave rise to the peak at 1235.67 cm^{-1} .

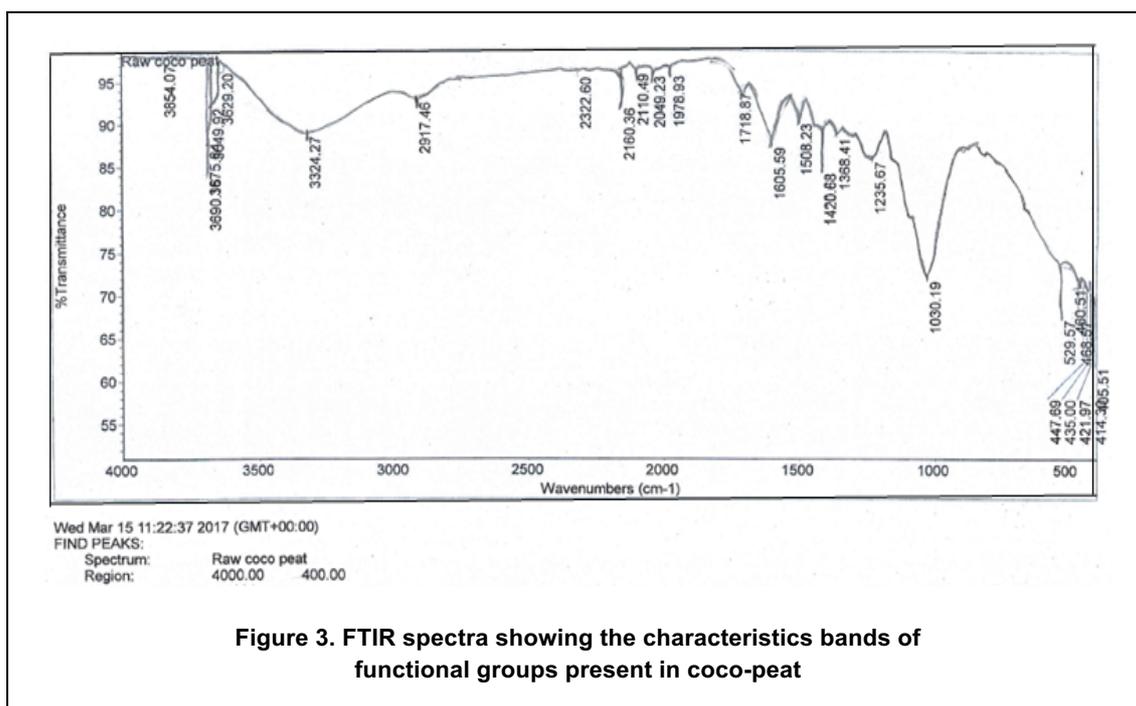


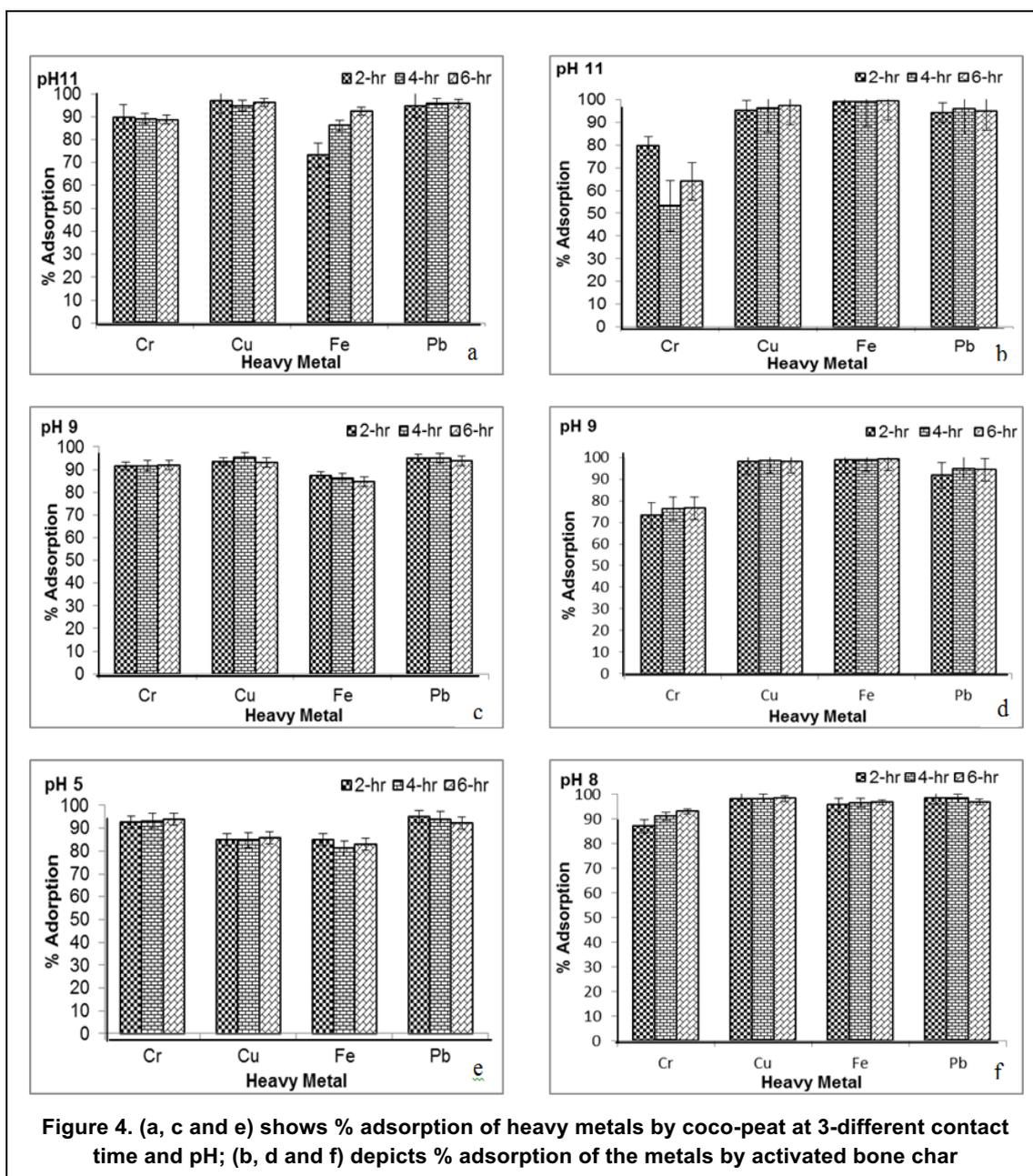
Figure 3. FTIR spectra showing the characteristics bands of functional groups present in coco-peat

Surface area and pore volume of adsorbents

The presence of lignin and cellulose as well as other impurities may have contributed to the low specific surface area ($1.2256 \pm 0.0133 \text{ m}^2/\text{g}$) with a very small pore volume as $3.588 \times 10^{-3} \text{ cm}^3/\text{g}$ for the coco-peat as measured by the BET method, whereas the surface area for activated bone char was found to be $99.6759 \pm 0.1793 \text{ m}^2/\text{g}$ with pore volume of $0.237874 \text{ cm}^3/\text{g}$. Although the surface area of the bone char in this study is relatively lower than $130.75 \text{ m}^2/\text{g}$ as reported by Rezaee et al., (2011), and the pore volume ($0.23787 \text{ cm}^3/\text{g}$) is also remarkably very small compared to the $8.8 \text{ cm}^3/\text{g}$ obtained in their study. However, the discrepancy in the pore volumes may be attributed to difference in particle size of bone char used in each study. As a rule of thumb, the larger surface area of bone char facilitates its high adsorption potentials for heavy metal ions. In contrast, to the surface area of coco-peat which was relatively small compared to that of bone char ($99.6759 \pm 0.1793 \text{ m}^2/\text{g}$) used as benchmark for this study. However, despite the low surface area of coco-peat, its adsorption ability for the heavy metals was found to be very high. Surprisingly, it was better than the bone char in terms of chromium and lead adsorption.

Heavy metal adsorption

The comparative analysis has been based on heavy metal adsorption efficiency between coco-peat and bone char are shown in Fig. 4. The Figures shows the percentage of heavy metals adsorbed under different pH conditions and contact time. This is with a view to determine the pH and contact time by which optimum adsorption is attained. The trend for Cr adsorption (%) as shown in Figs. 4 (a), (c) and (e) illustrates that coco-peat even though, non-activated, has a better affinity for Cr removal compared to the commercial activated bone char. The optimum adsorption of the coco-peat was observed as 90% after just 2-hours of residence time; whereas for the bone char, 79.5% Cr removal efficiency was achieved. The figures also indicate that adsorption of the Cr occurred at acidic or natural pH of both adsorbents compared to the pH 9 and 11. Although copper (Cu) appeared to be better adsorbed by the bone char as shown in Figs. 4(b), (d) and (f), with removal efficiency of over 98% at pH 9, coco-peat has proven to be effective with sorption efficiency of about 96% for just 2-hours of adsorption time at pH 11. The percentage of Fe removed by coco-peat (Fig. 4a) ranged between 73% and 87% after 2 hrs of adsorption at pH 9 and 11 respectively. Comparatively, Fe removal efficiency of bone char was 99% (Fig. 4b), which was significantly higher than those for coco-peat. Figs. 4a illustrates removal of Pb(II) ions by the coco-peat, which has higher sorptive affinity for lead (Pb^{+2}) ion with over 96% compared with the activated bone char with 94–95% efficiency after 2 hrs of contact time. At the end of this study, it was observed that at 2-hr of residence time and pH9, optimum adsorption of various heavy metals by the adsorbents were achieved.



Conclusion

The potential of using coco-peat, a low-cost biomass as an adsorbent for heavy metals removal from textile and tannery wastewater was investigated. The results show that coco-peat can remove Cr, Cu, Fe and Pb from textile and tannery wastewater with adsorption efficiency comparable with that of an activated bone char. The optimal conditions for effective adsorption were 2 hrs residence time and acidic pH for Cr, whereas pH 9 favours Cu, and Pb, and pH 11 for Fe. The results from this study suggest that the use of coco-peat can provide cost effective means for metal removal from industrial wastewaters. As such, it can be concluded that this novel wastewater treatment technique has met with the irrigation water requirements which were earlier discussed.

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