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Chemically Modified Biochar Derived from Cotton Stalks: Characterization And Assessing Its Potential for Heavy Metals Removal from Wastewater

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BIOCHAR derived from agricultural by-products is increasingly being recognized as a promising adsorbent material for wastewater remediation. This research is evaluating the effect of chemical treatment solutions on activating the sorption capacity of biochar derived from cotton stalks. The surface characteristics of chemically modified biochar (CMB) were investigated with scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDS) and fourier transform infrared (FTIR) spectroscopy. Using batch adsorption experiments, biochar pretreated with sulfuric acid (SAB), oxalic acid (OAB), sodium hydroxide (SHB) and the untreated biochar (UTB) were subjected to assess their removal efficiency of heavy metal ions (pb^{2+}, cd^{2+}, ni^{2+} and co^{2+}) as compared with activated carbon (AC). Biochar showed a higher sorption capacity of heavy metal ions as compared with AC. Biochar pretreated with acid solutions (SAB and OAB) exhibited a low removal efficiency of heavy metal ions as compared with other pretreatment solutions. shb was the most effective product for adsorption of pb^{2+} (44.64 mg g^{-1}), cd^{2+} (0.648 mg g^{-1}) and ni^{2+} (6.20 mg g^{-1}); however, UTB showed the highest adsorption capacity of co^{2+} (0.522 mg g^{-1}). These results are confirmed with ftir and sem-eds analyses, which showed an activation of the physiochemical properties of the modified biochar. The obtained results are highlighting the effectiveness of chemical pretreatment in biochar activation.

Keywords: Biochar, Cotton stalks, Chemical pretreatment, Surface characteristics, Heavy metals, Wastewater.

Introduction

In regions with water scarcity, the use of reclaimed wastewater resources for agricultural purposes is an option that is increasingly being investigated. In these circumstances, the use of reclaimed wastewater for irrigation enables freshwater to be directed towards more economically and socially valuable purposes (Winpenny et al. 2010). Traditional metal removal methods like chemical precipitation, chemical redox reactions, electrochemical treatment, membrane processes, and ion exchange are extremely expensive or inefficient, especially for large quantity and relatively very low concentrations (Volesky 1990). More research, therefore, is needed to capitalize some other methods such as biosorption, biological and ion-exchange processes over the classical remediation methods. This technique could be an

ideal treatment method in developing countries; because of the low cost processing, and the high removal efficiency of heavy metals. Recently, research has been directed to optimize efficient adsorbent materials from carbon-rich by-products (e.g. crop residues) with similar characteristics of activated carbon by the slow pyrolysis process.

Biochar refers to the C-rich residues of incomplete combustion of biomass under oxygen-limited conditions and at relatively low temperatures (<700°C; Lehmann and Joseph 2011). Biochar is increasingly receiving attention as a promising functional material in environmental and agricultural application as it has been credited with multiple benefits, including the ability to improve soil fertility, protect water quality, generate carbon neutral energy, increase agricultural output, contribute to carbon sequestration and remove pathogens

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(Laird et al. 2010). Recent studies have found that biochar contains many hollow-structured pore networks (i.e. micro-pores and macro-pores); thus, it has a potential to absorb and store chemical species including some of the common water pollutants such as heavy metal ions and hydrocarbon molecules (Kumar et al. 2011; Yao et al. 2011; Lu et al. 2012). Several investigations have been reported the removal efficiency of heavy metal ions by biochar adsorbents. Steam pyrolysed sugarcane bagasse pith showed a higher adsorption capacity of 140.85 mg g-1 for the removal of Ni2+ ions from aqueous solutions Krishnan et al. (2011). Another investigation showed that biochar derived from anaerobically digested sugarcane bagasse was more effective than activated carbon for the removal of Pb2+ ions from wastewater (653.9 mmol kg-1 for biochar vs. 395.3 mmol kg-1 for activated carbon) (Inyang et al., 2011). The removal of Cu2+ and Cd2+ from aqueous solutions was close to 100% using biochar produced from switchgrass via hydrothermal carbonization (Regmi et al. 2012).. Authors also added that adsorption capacities of Cu2+ and Cd2+ ions by the hydrothermal carbonized biochar were higher than those of powdered activated carbon (31 and 34 mg g-1 for biochar vs. 1.8 and 1.5 mg g-1 for activated carbon, respectively).

Several feedstock materials have been investigated to produce biochar for the removal of water contaminants e.g. sugar beet tailings (Yao et al., 2011), sugarcane bagasse (Inyang et al., 2011), rice straw (Jiang et al., 2012) and wheat straw (Song et al., 2012); however, little is known about cotton stalks-based biochar. Cotton is one of the most important cultivated crops in Egypt. The "Egyptian cotton" is a peculiar type of cotton that is characterized by high quality, and gained a world-wide reputation for more than a century and a half as being of the highest lint quality among world cottons. The annual production of cotton fiber is estimated as 4940 ton with by-products of approximately 1.6 million tons cotton stalks (Abdel-Salam and Negm 2009). Normally removed from the field at harvest time and stored as stock feed, or burnt in the field, crop residues in Egypt are managed as in most developing countries (Abdel-Mohdy et al., 2009). As cotton stalks are not favorable feed for livestock, farmers regularly burn huge amounts of cotton stalks in the field. Subsequently, substantial amounts of greenhouse gases (e.g. carbon dioxide, carbon

monoxide, methane, nitrogen oxides and sulfur dioxide) are emitted to the atmosphere (Streets et al., 2003). Recycling crop resides to value added products is, therefore, an urgent need in order to protect the environment from different hazards.

Chemical pretreatment with base solutions, mineral and organic acid solutions, organic compounds, oxidizing agents, dyes, etc. have been investigated for enhancing the adsorption capacity of biosorbent materials (Mosa et al., 2011; Wang et al., 2015; Inyang et al., 2016; Mosa et al., 2016a). The chemical pretreatment modifies the surface characteristics/groups of the biosorbent material either by removing or masking the groups or by exposing more metal-binding sites (Vieira and Volesky 2000). The chemical pretreatment of biochar with KOH led to increase the internal surface area at least 50 times than that of the precursor, in addition to maximizing the micro-porous structure, which is confirmed by scanning electron microscopy analysis (Azargohar and Dalal 2006). Characterization measurements showed also that H2O2 modification increased the oxygen-containing functional groups, particularly carboxyl groups, on the biochar surfaces (Xue et al., 2012).

In this work, biochar produced from cotton stalks was pretreated with different chemical pretreatment solutions (i.e., sulfuric acid, oxalic acid and sodium hydroxide) as compared with the untreated biochar in order to increase its metal-binding capacity. We hypothesized that the chemical pretreatment of biochar could increase functional groups on biochar surfaces, and thus enhance its ability to remove heavy metals from aqueous solutions.

Materials and Methods

Materials

The raw feed stock of biochar production, cotton stalks (0.51- mm), were obtained from El-Gimiza Agricultural Research Farm, Ministry of Agriculture, Egypt. The feedstock material was oven dried at 70°C until the constant of weight. Briefly, a 200 g was placed in a beaker covered with a watch glass to create oxygen-limited conditions during biochar production. Pyrolysis process was carried out by heating in a muffle furnace at 550 °C for 2 h. The produced biochar was ground manually using a ceramic mortar, to increase the total surface area, and passed through

a 0.25-mm sieve. The chemical pretreatment of biochar was carried out by shaking biochar with 0.1 M of oxalic acid, sulfuric acid or sodium hydroxide (1:100 W/V) at an agitation rate of 150 rpm for 4 h. After shaking, the chemically modified biochar (CMB) was filtered, rinsed with tap water followed by double distilled water (to remove the excess of chemical solutions) and oven dried at 70°C for 24 h. A commercial activated carbon of lignite origin was obtained from Sigma-Aldrich Chemie GmbH, Germany to represent the conventional remediation treatment.

Synthetic solutions of heavy metals (i.e. Pb^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+}) were prepared from Merck analytical grade stock standards of 1,000 mg L^{-1} by diluting with double distilled water to the required concentrations. According to FAO, the recommended maximum concentrations of Pb^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+} in irrigation water are 5.0, 0.01, 0.20 and 0.05 mg L^{-1}, respectively (Ayers and Westcot 1985). The first concentration of synthetic wastewater solutions was prepared to be higher than the recommended maximum concentration limits, and concentrations of heavy metal ions in other synthetic wastewater solutions were prepared to be approximately 2, 4, 6 and 10-folds from the

TABLE 1. Initial concentration of heavy metal ions in different synthetic wastewater solutions

Synthetic wastewater solutions	Heavy metal ions concentration (mg L^{-1})			
	Pb^{2+}	Cd^{2+}	Ni^2	Co^{2+}
First	10	0.1	1	0.1
Second	20	0.2	2	0.2
Third	40	0.4	4	0.4
Fourth	60	0.6	6	0.6
Fifth	80	1	10	1

first concentration. The initial concentrations of heavy metal ions in different synthetic wastewater solutions are listed in Table 1.

Biochar properties

Elemental analysis of biochar was carried out according to the AOAC method of acid digestion for the multi-elemental analysis by Inductivity Coupled Plasma Spectrophotometer (ICP). Subsamples (0.2 g) were acid digested using the mixture of HNO3 (65%) and H2O2 (30%) in a microwave digestion apparatus (model MLS GmbH, Germany). Inorganic metal ions concentration was determined using ICP (model ICP/CIROS CCD SOP, Germany). Carbon and nitrogen were determined using CNS analyzer

TABLE 2. Elemental analysis of the raw cotton stalks and the chemically modified biochar.

Raw feedstock and biochars	(%)		(mg g⁻¹)										(mg kg⁻¹)			
	C	N	P	Ca	K	Na	Mg	S	Fe	Mn	Zn	Cu	Co	Pb	Cd	Ni
Raw cotton stalks	48.1	1.19	1.02	6.63	24.25	14.12	1.71	1.98	215	16	14	11	0.74	14.23	0.32	1.12
UTB	77.5	0.95	0.38	1.22	7.74	2.49	4.65	2.63	669	80	46	29	0.26	1.95	0.18	0.49
OAB	65.5	0.81	0.15	1.17	4.18	2.83	3.48	3.00	452	61	27	18	0.22	1.35	0.11	0.41
SAB	61.3	0.70	0.12	0.43	3.81	2.35	2.99	8.28	731	88	38	33	0.32	1.46	0.22	0.55
SHB	73.5	0.90	0.32	1.36	7.51	11.77	3.02	2.86	689	76	32	28	0.28	1.65	0.16	0.51

(model Carlo Erba NA 1500 Series 2, Italy). Elemental analysis of the raw cotton stalks and the produced biochar is illustrated in Table (2).

The surface structure of CMB was analyzed by scanning electron microscopy imaging analysis (SEM) using a JEOL-TEM 100 CX scanning microscope (Japan). Elemental analysis of biochar surfaces was determined simultaneously with the SEM at the same surface locations using energy dispersive X-ray spectroscopy (JEOL-JSM 5300, Japan). Characterization of the surface organic functional groups presented in biochar samples was carried out using Fourier Transform Infrared (FTIR) analysis. For FTIR analysis, biochar was mixed with KBr at the ratio of 1:10, and the spectra of biochar samples were measured using a Thermo Nicolet iS10 FTIR Spectrometer, USA.

Adsorption isotherm
In batch adsorption experiments, 0.1 g of biochar or activated carbon was shaken with 50 mL of synthetic wastewater solutions in a 100-mL plastic bottle at an agitation rate of 150 rpm for 4 h. Each sample was replicated four times, and controls were used without the biosorbent material to distinguish between possible metal precipitation and actual metal adsorption. Samples were filtered through a 0.22 μm Millipore filter, and metal ions concentration was determined using ICP. The removal efficiency (E) of heavy metal ions was calculated as follows:

$$E = \frac{C_i - C_e}{C_i} \times 100$$

where C_i and C_e are the initial and the final equilibrium concentration of heavy metals (mg L−1).

Other cations, which could be released into the solution through exchange reactions, were determined using ICP to measure the released metal ions into the solution during the competitive biosorption reactions.

Langmuir isotherm model was subjected to simulate the adsorption of heavy metal ions on biochar and activated carbon:

$$\frac{C_e}{q_e} = \frac{1}{K\,q_{max}} + \frac{C_e}{q_{max}}$$

where C_e is the equilibrium concentration (mg L−1), q_e is the amount of the metal ion adsorbed at equilibrium (mg g−1), K is the equilibrium adsorption constant (L mg−1), which is related to the affinity of the binding sites, and q_{max} is the maximum amount of metal ion per unit mass of biosorbent when all binding sites are occupied (mg g−1). The amount of the metal ion adsorbed at equilibrium (q_e) was determined by employing the mass balance as follows:

where q_e is the equilibrium metal uptake (mg g−1), C_i and C_e are the initial and the final metal concentration (mg L−1), respectively, V is the solution volume (L), and m is the mass of adsorbent material (g).

All sorption studies were carried out in duplicates, and additional analyses were performed whenever two measurements showed a difference of more than 5%.

Results and Discussion
Elemental analysis of chemically modified biochar
During the pyrolysis process that generates biochar, some elements are exposed to lost by volatilization; other elements remain concentrated in biochar (Table 2). The elemental analysis of biochars derived from cotton stalks showed high carbon content. This rich content of carbon in the produced biochar is introducing cotton stalks as a promising feedstock for biochar production. The chemical pretreatment with acid solutions reduced carbon content of the produced biochar as compared with UTB. This could be due to the evolution of carbon oxides (CO and CO_2) during the pretreatment process (Kuwata et al., 2009). After being converted to biochar by pyrolysis process, N content of biochar was lower than that of the raw cotton stalks. This could be attributed to the loss of N compounds through evolution of N-oxides, especially NH3. Nitrogen concentration in SAB was lower than other biochar types, presumably due to the partial digestion of organic nitrogen compounds by the diluted H_2SO_4. Phosphorus and calcium concentrations in SAB were also less than other biochar types. This might be due to increasing the solubility of calcium phosphate and calcite precipitates of biochar during the pretreatment process. The significant reduction of K and Na concentrations in biochar as compared with the feedstock materials is attributed to the fact that K

and Na are not involved in the organic compounds of plant (Marschner 1995). Substantial amounts of these elements, therefore, are lost during pyrolysis and chemical pretreatment of biochar. It is noticeable that the chemical pretreatment with NaOH led to a high increase in Na concentration in SHB as compared with other biochar types. Unlike other macro-elements, Mg and S showed a substantial increase in their concentrations after pyrolysis process as compared with the raw cotton stalks. Concerning micro-element concentrations in biochar, it is noticeable that there were considerable increases in concentrations of Fe, Mn, Zn and Cu; however, concentrations of Co, Pb, Cd, and Ni showed a reduction as compared with the raw feedstock. This reduction is mainly attributed to the volatilization of these micro-elements during the pyrolysis (Kistler 1987; Lu et al., 2004; Wei et al., 2012).

SEM-EDS analysis

During the chemical pretreatment of carbonaceous materials, a large number of micro-pores are formed to increase the adsorption capacity of the activated material (Inagaki 2009). The SEM photographs showed that there are considerable cracks and attached fine particles forming a system of complicated micro-pore networks (Fig.1). The SEM analysis of UTB showed a compact rigid particle structure, while OAB and SAB showed more fragile and distorted bundles. Biochar pores were blocked by potassium and basic compounds before the chemical pretreatment; however, chemical pretreatment with acid/alkali solutions removed considerable amounts of these compounds and exposed the active surfaces of biochar. These results are confirmed with EDS analysis. On the other hand, the SEM photographs demonstrated that the alkali pretreatment with sodium hydroxide caused caking and agglomeration of SHB as compared with OAB and SAB.

Consistent with the analytical data of ICP, the EDS spectra also indicated that the chemical pretreatment of biochar using acid solutions was associated with low potassium peaks as compared with UTB (Fig. 1). On the other hand, the EDS spectra of SAB showed high peaks of calcium and sulfur. Calcium is one of the major inorganic elements accumulated on the surfaces of granular carbonaceous materials by precipitating mainly as calcium carbonate (Lee et al., 2003). This accumulation of calcium led to decrease the

adsorption capacity of SAB. In addition, the high content of sulfur on SAB (mainly existed as elemental sulfur) led to narrow micro-pores of biochar surfaces by forming sulfur depositions in these micro-pores (Feng et al., 2006). This was further confirmed by the SEM analysis, which showed evidence of mineral crystals on biochar surfaces. These crystals are mainly calcite and sulfur as evidenced in the EDS spectrum, which showed high peaks of calcium and sulfur. The OAB showed an increase in Si peak as compared with other pretreatment methods. This could be attributed to the acceleration of the dissolution rate of silicates in the presence of oxalic and other simple carboxylic acids as compared with inorganic acids under the same pH (Stillings et al., 1996; Cama and Ganor 2006). The increment in the dissolution rate of silicates increased Si ions in the solution, which are more able to compete for biochar adsorption sites than other cations. Silicon content, therefore, increased on OAB surfaces.

Surface functional groups

The FTIR analysis demonstrated the functional groups presented on biochar surfaces, and the effect of different pretreatment methods on the activation of these groups. As shown in Fig. (2), the infra-red spectra of the different pretreated biochar types are comparable; however, there are some changes in the functional groups resulted from the chemical activation methods. The strong absorption bands between 3300 -3500 cm-1 indicated the presence of hydroxyl and amino groups. Comparing with other biochar types, UTB and SHB were associated with strong absorption bands at 3395.9 and 3424.7 cm-1, respectively, which corresponds to hydroxyl or amino groups. The C-H stretching region ranged between 2900 - 3000 cm-1 in different biochar types. The strong absorption at 2925.7, 2931.2 and 2935.3 illustrated the activation of C-H stretching groups on UTB, SAB and SHB surfaces, respectively. This spectrum, however, was very low with OAB. The stretching vibrations of carbonyl and carboxyl groups were detected at high absorption with UTB and OAB at 1713.4 and 1726.1 cm-1, respectively. This spectrum became lower with SAB and SHB. The peaks observed at 1460.6, 1451.0, 1457.9 and 1451.7 with UTB, OAB, SAB and SHB, respectively, corresponded to aromatic C=C ring stretching. The peaks located at 1021.9, 1032.8, 1043.7 and 1057.9 cm-1 for UTB, OAB, SAB and SHB, respectively, assigned to ─CO stretching vibration of the alcoholic groups.
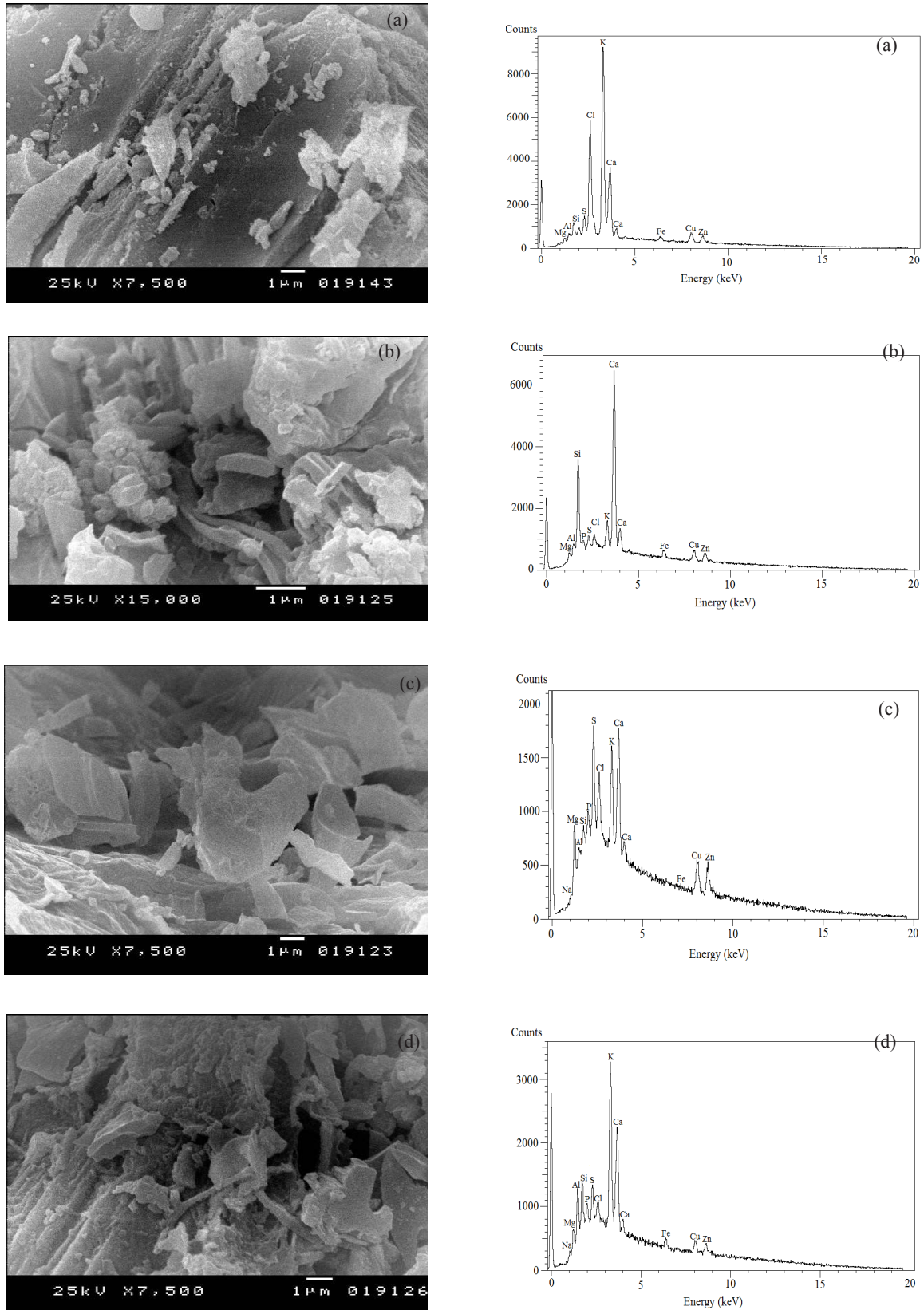
Fig. 1. SEM and EDS spectra of UTBB (a), OAB (b), SAB (c) and SHB (d).
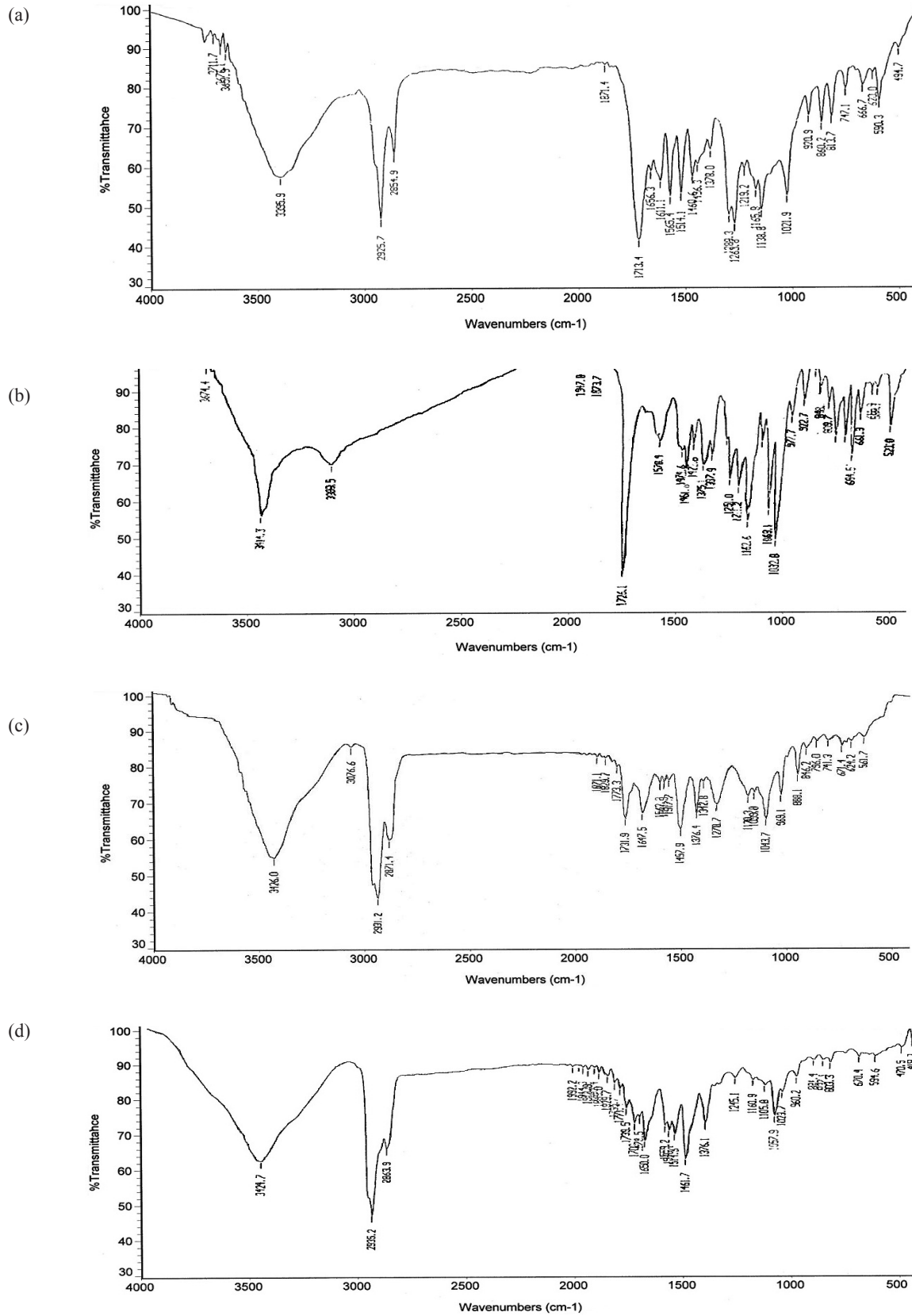
Fig. 2. FTIR spectra of DWB (a), OAB (b), SAB (c) and SHB (d).

Active functional groups have been characterized based on previously reported investigations (Inyang et al., 2010; Dong et al., 2011; Neto et al., 2011; Mosa et al., 2016b; Luo et al., 2017).

Removal of heavy metal ions from synthetic wastewater solutions

The removal efficiency of heavy metal ions by CMB was higher than their removal by AC, especially at high concentrations (Fig. 3). The removal efficiency decreased as the initial concentration increased in aqueous solutions due to the saturation of binding sites at higher initial concentrations leaving more of these ions un-adsorbed in the solution. The removal efficiency of heavy metal ions by CMB was more than 99% at low concentrations. This removal efficiency decreased slightly at higher concentrations; however, it was more than 90% in most cases. Meanwhile, the removal efficiency of Pb^{2+} and Ni^{2+} ions by activated carbon was very low at high concentrations.

As compared with SHB and UTB, the acid pretreatment with sulfuric acid and oxalic acid led to a significant decrease on the removal efficiency of heavy metals, especially Ni^{2+} ions. According to the SEM-EDS analysis, the formation of calcite and sulfur on OAB and SAB surfaces might cause

narrow micro-pores of biochar surfaces by forming depositions in these micro-pores. In addition, the high silicon content on OAB surfaces could contribute on decreasing the removal efficiency of metal ions as the tetravalent cations are difficult to exchange by divalent cations. SHB exhibited the highest removal efficiency of Pb^{2+}, Cd^{2+} and Ni^{2+} ions; meanwhile, UTB recorded the highest removal efficiency of Co^{2+} ions.

Adsorption isotherm

The linearity of plots Ce/qe versus Ce suggested the applicability of Langmuir isotherm for this study (Fig. 4). This appeared in the high correlation coefficient values exhibited by Langmuir isotherm; with R^2 exceeding 0.90% in most cases (Table 3). Values of q_{max} and K were determined from the slopes and intercepts of the respective plots. The maximum Pb^{2+} sorption onto SHB (44.64 mg g-1) was slightly higher than other biochar materials, and it was more than double that of AC (17.39 mgg-1). The maximum Cd^{2+} sorption by different adsorbent materials was comparable, with superiority for SHB. The SHB also had the highest sorption capacity of Ni^{2+} (6.20 mg g-1); this was more than double of OAB and SAB, and more than
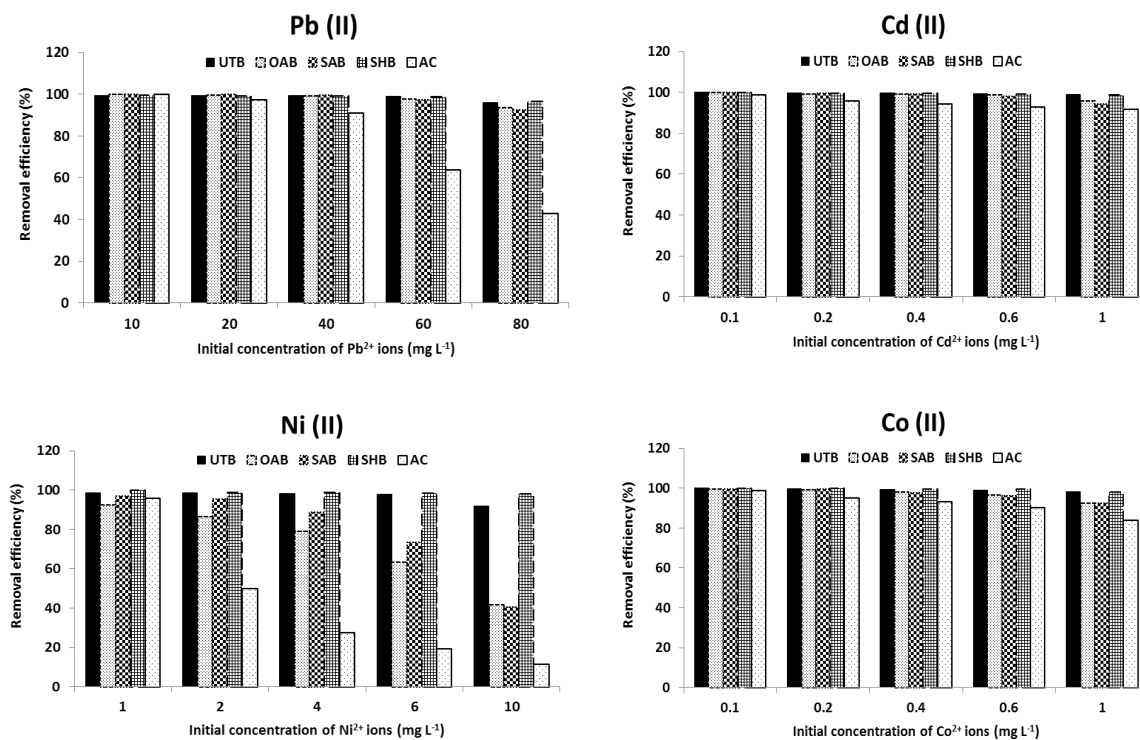

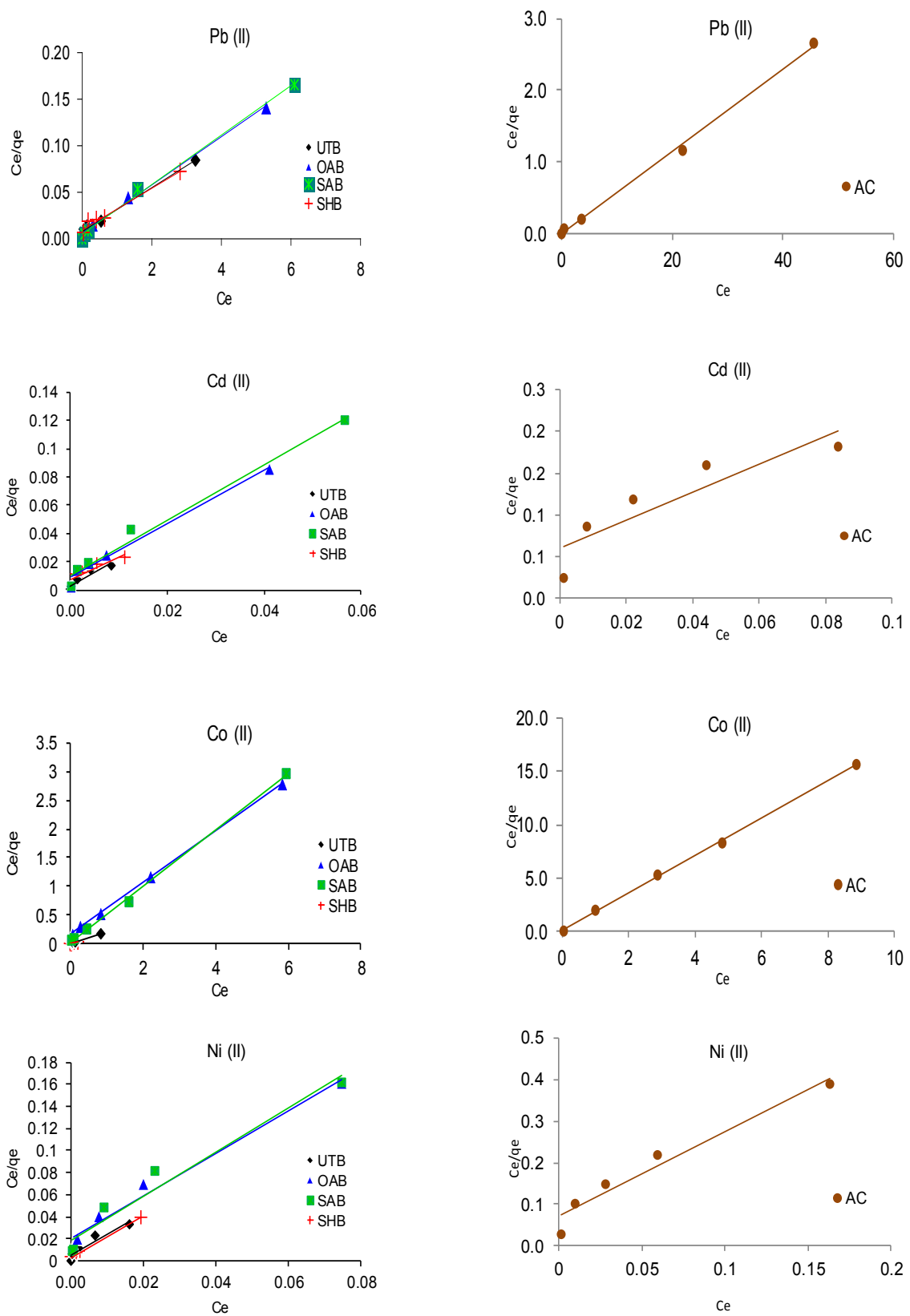Fig. 3. The removal efficiency (%) of heavy metal ions by different adsorbent materials.

Fig. 4. Linearization of Langmuir adsorption isotherms for the adsorption of heavy metal ions on different ad-
sorbent materials.

TABLE 3. Summary of isotherm model parameters.

Heavy metals	UTB			OAB			SAB			SHB			AC		
	K (L mg⁻¹)	q_{max} (mg g⁻¹)	R^2	K (L mg⁻¹)	q_{max} (mg g⁻¹)	R^2	K (L mg⁻¹)	q_{max} (mg g⁻¹)	R^2	K (L mg⁻¹)	q_{max} (mg g⁻¹)	R^2	K (L mg⁻¹)	q_{max} (mg g⁻¹)	R^2
Pb	2.90	42.55	0.997	3.97	38.76	0.997	5.78	37.59	0.996	2.26	44.640	0.983	4.91	17.390	0.997
Cd	653.17	0.53	0.879	201.78	0.53	0.984	189.09	0.51	0.986	214.43	0.648	0.835	28.28	0.590	0.811
Ni	8.66	5.25	0.998	2.86	2.21	0.999	18.04	2.05	0.999	11.87	6.200	0.777	16.72	0.572	0.999
Co	358.15	0.54	0.913	93.58	0.52	0.985	107.89	0.50	0.961	709.37	0.522	0.989	28.61	0.491	0.953

10-folds higher than AC. Unlike other heavy metals, Co^{2+} sorption capacity by UTB was slightly higher than other adsorbent materials (0.537 mg g-1).

Desorption of metal ions

The desorption of metal ion cations increased with increasing the initial concentration of Pb^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+} in synthetic wastewater solutions (Fig. 5). Desorption of K^+ was higher than other cations. This could be attributed to the fact that K is not involved in organic constituents of plants (Azargohar and Dalal 2006). The highest desorption of K^+ was associated with SHB; conversely, AC showed the lowest desorption of K^+. Relatively lower concentrations of Ca^{2+} were detected after carrying out the adsorption process as compared with K^+ ions. A higher desorption of Ca^{2+} ions, however, was recorded with SAB, which confirmed with the results of EDS analysis. The desorption of Mg^{2+} and Na^+ ions was comparable among different biochar types with a higher desorption of Na^+ ions with SHB. This is also confirmed with the data of EDS analysis.

Although the desorption of Fe^{2+} ions was comparable in different biochar types, a variation in Mn^{2+} ions desorption was observed indicating a significant effect of the pretreatment methods. Manganese complexes in different organic compounds are principally involved in electrostatic forces between the hydrated metal ion and oxygen-containing ligands. These complexes are easily disrupted by proton or metal exchange ions during the pretreatment process (Mosa et al., 2011). The chemical pretreatment, especially with acid solutions, led to considerable cracks in biochar surfaces, and appearance of internal surfaces. This could be the reason of the high desorption of Mn^{2+} as compared with UTB. Unlike other metal ions, desorption of Zn^{2+} and Cu^{2+} was not detected; indicating a strong binding of these elements by organic matter molecules.

Conclusions

As cotton stalks is an abundant agricultural byproduct, cotton stalks-based biochar could be produced at low cost and relatively little processing. We hypothesized that the chemical pretreatment with mineral/organic acids and alkali solutions could improve the adsorption capacity of biochar surfaces. The SEM-EDS and FTIR analysis showed an improvement in surface adsorption characteristics due to the chemical pretreatment with sodium hydroxide. The

chemical pretreatment with acid solutions (oxalic and sulfuric acids) was associated with narrow micro-pores formation on biochar surfaces by forming calcite and sulfur depositions in these micro-pores. The removal efficiency of heavy metal ions by CMB was significantly higher than its removal by AC, and SHB was the most efficient adsorbent. Although further studies is needed to prove its ability for heavy metals remediation and mitigating its accumulation in plant tissues, biochar filters could be considered as a promising technique for wastewater remediation prior to irrigation.
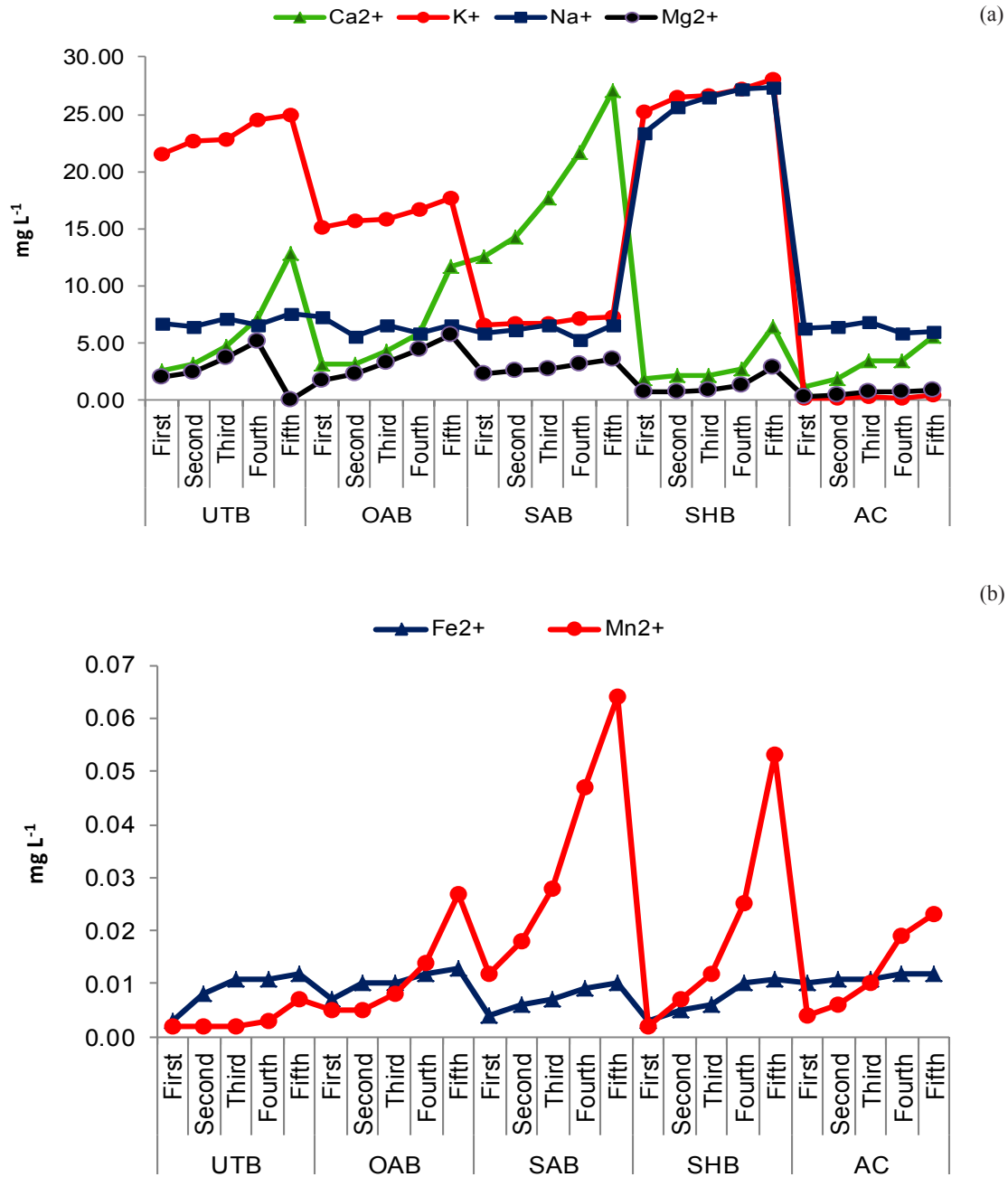
Fig. 5. Desorption of macro-elements (a) and micro-elements (b) after carrying out the adsorption experiment.

(130-055-D1433) and Mansoura University is gratefully appreciated.

References

Abdel-Mohdy, F.A., Abdel-Halim, E.S., Abu-Ayana, Y.M., El-Sawy, S.M. (2009) Rice straw as a new resource for some beneficial uses, *Carbohyd. Polym.* **75,** 44–51.

Abdel-Salam, M.E., Negm, A.M. (2009) *The Egyptian Cotton; current constraints and future opportunities.* Textile Industries Holding Co. Modern Press - Alexandria-Egypt.

Ayers, R.S., Westcot, D.W. (1985)Water quality for agriculture. *Irrigation and Drainage Paper* No.**29,** FAO, Rome.

Azargohar, R., Dalal, A.K. (2006). Biochar as a precursor of activated carbon, Appl. *Biochem. Biotech.* **129-132,**762-773.

Cama, J., Ganor, J. (2006) The effects of organic acids on the dissolution of silicate minerals: A case study of oxalate catalysis of kaolinite dissolution. *Geochim. Cosmochim. Ac.* **70,** 2191-2209.

Dong, X., Ma, L.Q., Li, Y. (2011) Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing, *J. Hazard. Mater.* **190,** 909–915.

Feng, W., Kwon, S., Feng, X., Borguet, E., Vidic, R. (2006). Sulfur impregnation on activated carbon fibers through H2S oxidation for vapor phase mercury removal, *J. Environ. Eng.* **132,** 292-300.

Inagaki, M. (2009). Pores in carbon materials-importance of their control, *New Carbon Mater.* **24,**193-232.

Inyang, M., Gao, B., Ding, W., Pullammanappallil, P., Zimmerman, A.R., Cao, X. (2011). Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse, Separ. Sci. *Technol.* **46,** 1950–1956.

Inyang, M., Gao, B., Pullammanappallil, P., Ding, W., Zimmerman, A.R. (2010). Biochar from anaerobically digested sugarcane bagasse, *Bioresource Technol.* **101,** 8868–8872.

Inyang, M.I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., Pullammanappallil, P., Ok, Y.S., Cao, X. (2016). A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. *Critical Reviews in Environmental Science and Technology* **46,** 406-433.

Jiang, T., Jiang, J., Xu, R., Li, Z. (2012). Adsorption of Pb(II) on variable charge soils amended with rice-straw derived biochar, *Chemosphere* **89,** 249–256.

Kistler, R.C., Widmer, F., Brunner, P.H. (1987).

Behavior of chromium, nickel, copper, zinc, cadmium, mercury, and lead during the pyrolysis of sewage sludge, *Environ. Sci. Technol.* **21,** 704–708

Krishnan, K.A., Sreejalekshmi, K.G., Baiju, R.S. (2011). Nickel(II) adsorption onto biomass based activated carbon obtained from sugarcane bagasse pith, *Bioresource Technol.* **102,** 10239-10247.

Kumar, S., Loganathan, V.A., Gupta, R.B., Barnett, M.O. (2011). An Assessment of U(VI) removal from groundwater using biochar produced from hydrothermal carbonization, *J. Environ. Manage.* **92,** 2504-2512.

Kuwata, K., Saito, Y., Shida, S. (2009). Intercalation of wood charcoal with sulfuric acid. *J. Wood Sci.* **55,** 154-158.

Laird, D., Fleming, P., Wang, B., Horton, R., Karlen, D. (2010). Biochar impact on nutrient leaching from a Midwestern agricultural soil, *Geoderma* **158,** 436–442.

Lee, S., Nishijima, W., Lee, C., Okada, M. (2003). Calcium accumulation on activated carbon deteriorates synthetic organic chemicals adsorption, *Water Res.* **37,** 4631–4636.

Lehmann, J., Joseph, S. (2009) *Biochar for Environmental Management: Science and Technology,* Earthscan, Ltd.: London.

Lu, H., Chen, H., Li, W., Li, B. (2004) Occurrence and volatilization behavior of Pb, Cd, Cr in Yima coal during fluidized-bed pyrolysis, *Fuel* **83,** 39–45.

Lu, H., Zhang, W., Yang, Y., Huang, X., Wang, S., Qiu, R. (2012) Relative distribution of Pb2+ sorption mechanisms by sludge-derived biochar, *Water Res.* **46,** 854-862.

Luo, X., Yu, L., Wang, C., Yin, X., Mosa, A., Lv, J., Sun, H. (2017). Sorption of vanadium (V) onto natural soil colloids under various solution pH and ionic strength conditions. *Chemosphere.* **169,** 609-6017.

Marschner, H. (1995). *Mineral Nutrition Of Higher Plants,* 2nd edn. Academic, London.

Mosa, A., El-Banna, M.F., Gao, B. (2016b). Biochar filters reduced the toxic effects of nickel on tomato (Lycopersicon esculentum L.) grown in nutrient film technique hydroponic system. *Chemosphere* **149,** 254-262.

Mosa, A., El-Ghamry, A.M., Trüby, P., Gao, B., Omar, M., Elnaggar, A., Li, Y. (2016a). Chemo-mechanical modification of cottonwood for Pb2+ removal from aqueous solutions: sorption mechanisms and potential application as biofilter in drip-irrigation.

Chemosphere. **161,** 1-9.

Mosa, A.A., El-Ghamry, A.M., Trüby, P.A. (2011). Chemically modified crop residues as a low-cost technique for the removal of heavy metal ions from wastewater. *Water Air Soil Poll, 217,* 637-647.

Neto, V.O.S., Oliveira, A.G., Teixeira, R.N.P., Silva, M.A.A., Freire, P.T.C., Keukeleire, D.D., Nascimento, R.F. (2011). Use of coconut bagasse as alternative adsorbent for separation of copper (II) ions from aqueous solutions: isotherm, kinetics and thermodynamic studies, *Bioresources* **6,** 3376-3395.

Regmi, P., Moscoso, J.L.G., Kumar, S., Cao, X., Mao, J., Schafran, G. (2012). Removal of copper and cadmium from aqueous solution using switchgrass biochar produced via hydrothermal carbonization process, *J. Environ. Manage.* **109,** 61-69

Song, Y., Wang, F., Bian, Y., Kengara, F.O., Jia, M., Xie, Z., Jiang, X. (2012). Bioavailability assessment of hexachlorobenzene in soil as affected by wheat straw biochar, *J. Hazard. Mater.* **217-218,** 391-397

Stillings, L.L., Drever, J.I., Poulson, S.R., Brantley, S.L., Yanting, S., Oxburgh, R. (1996). Rates of feldspar dissolution at pH 3-7 with 0-8 m M oxalic acid, *Chem. Geol.* **132,** 79-89.

Streets, D.G., Yarber, K.F., Woo, J.H., Carmichael, G.R. (2003). Biomass burning in Asia: annual and seasonal estimates and atmospheric emissions, *Global Biogeochem. Cy.* **17,** 1099–1118.

Vieira, R.H.S.F., Volesky, B. (2000). Biosorption: a solution to pollution? *Internatl Microbiol.* **3,** 17–24.

Volesky, B. (1990). *Biosorption Of Heavy Metals,* Boca Raton: CRC.

Wang, S., Gao, B., Li, Y., Mosa, A., Zimmerman, A., Ma, L., Harris, W., Migliaccio, K. (2015). Manganese Oxide- modified biochars: Preparation, characterization, and sorption of arsenate and lead. *Bioresource Technology.* **181,** 13-17.

Wei, X., Zhang, G., Cai, Y., Li, L., Li, H. (2012). The volatilization of trace elements during oxidative pyrolysis of a coal from an endemic arsenosis area in southwest Guizhou, China, *J. Anal. Appl. Pyrol.* **98,** 184-193.

Winpenny, J., Heinz, I., Koo-Oshima, S., Salgot, M., Collado, J., Hernandez, F., Torricelli, F. (2010). *The Wealth Of Waste: The Economic Of Wastewater Use In Agriculture,* Paper No 35. FAO, Rome.

Xue, Y., Gao, B., Yao, Y., Inyang, M., Zhang, M., Zimmerman, A.R., Ro, K.S. (2012). Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests, *Chem. Eng.*

J. **200–202,** 673–680.

Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X., Pullammanappallil, P., Yang, L. (2011). Biochar derived from anaerobically digested sugar beet tailings: Characterization and phosphate removal potential. *Bioresource Technol,* **102,** 6273–6278.