

Calcined biomass-modified bentonite clay for removal of aqueous metal ions



Bamidele I. Olu-Owolabi^a, Alimoh H. Alabi^{a,*}, Emmanuel I. Unuabonah^b, Paul N. Diagboya^c, Leonard Böhm^d, Rolf-Alexander Düring^d

^a Department of Chemistry, University of Ibadan, Ibadan, Nigeria

^b College of Natural Sciences, Department of Chemical Sciences, Redeemer's University, Ogun State, Nigeria

^c Landmark University, Omu-Aran, Kwara State, Nigeria

^d Institute of Soil Science and Soil Conservation, Justus Liebig University, Giessen, Germany

ARTICLE INFO

Article history:

Received 2 November 2015

Received in revised form 25 January 2016

Accepted 31 January 2016

Available online 2 February 2016

Keywords:

Carica papaya seed

Pine cone

Bentonite

Calcination

Biomass-modified clay

Metals

ABSTRACT

Recent studies have shown that kaolinite clay modified with biosorbents are promising low cost adsorbents for the removal of metals from aqueous solution because the resultant composites have higher adsorption capacities, and hence a better aqueous metal ions removal efficiencies. However, some clay properties suggest that not all such modifications enhance adsorption capacity. In this study, bentonite (BEN) clay was calcined after modification with *Carica papaya* seeds or pine cone to obtain *C. papaya*-modified bentonite (CPB) and pine cone-modified bentonite (PCB). The efficiencies of these adsorbents for the removal of Pb(II), Cu(II) and Cd(II) ions from aqueous solutions were studied as a function of pH, time, sorbate concentration and temperature. X-ray diffraction results showed that CPB and PCB had lattice structure as BEN, but reductions in the surface areas of CPB and PCB were observed. Adsorption results showed that pH did not significantly affect removal of aqueous metal ions between pH 3 and 7. The adsorption fitted pseudo-second order ($r^2 \geq 0.966$) and intra-particle diffusion models and indicated mainly surface phenomena involving sharing of electrons between the adsorbent surfaces and the metal ion species. Unlike Cu(II) and Cd(II), Pb(II) adsorption reduced in CPB and PCB indicating that not all calcined biomass-clay composites have enhanced aqueous metal adsorption efficiency. However, undesired properties such as adsorbent bleeding were removed and mechanical strength enhanced while easier separation of the adsorbents from solution as compared to the raw bentonite was observed.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The search for cheap, efficient and accessible water treatment technologies cannot be overemphasized. For instance, recent anthropogenic activities have enormously contributed to toxic substances in water bodies leading to unprecedented water pollution and impacting negatively on the ecosystem [1–3]. Hejazi et al. [4] have reported that the nature of this impact is enormous and worldwide; for example over one billion people lack reliable access to clean water and 2.3 billion people of the global population live in water-stressed areas, a number that will increase by 52% in 2025.

Removal of toxic chemical substances by adsorption using low-cost adsorbents is a method of choice in the water treatment process. This is due to the several techno-economic and

environmental advantages associated with low-cost adsorbents when compared to other water treatment techniques; cheap, easy to obtain, process and use, available in abundance as waste or nuisance, good efficiency of adsorption and environmentally friendly [5–7]. Several low cost adsorbents such as biological materials [6–15], nanomaterials [16,17] and clays [5,18–24] have been investigated. However, most of these adsorbents suffer from limitations such as low efficiency of pollutant removal, technicality, low stability, bleeding, low mechanical strength, non-durability and/or poor re-usability, thus limiting their potential for applications. These have led to the search for more efficient and lower cost adsorbents.

In order to circumvent these limitations, modification techniques such as intercalation [25,26] pillaring [5,27], organic surface treatment [28,29], thermal activation [19,30], acid-alkaline treatment [5], and others have been used. However, the cost and efficiencies of these techniques are still major challenges.

Synergistic combinations of clays and biosorbents (both being low cost adsorbents) are beginning to receive attention [31]

* Corresponding author.

E-mail address: helenalabie3@yahoo.com (A.H. Alabi).

because these low cost sorbents are generally believed to increase the subsequent properties of the new adsorbents. This is achieved by combining individual characteristics of each composite to yield fewer final adsorbent limitations than the pure individual low cost adsorbents. Such synergistic combinations may lead to better sorbent properties such as high cation exchange capacity (CEC), reduce/eliminate bleeding, enhanced mechanical strength, pore size and consequently higher adsorption efficiency, better stability and durability, re-usability, sometimes larger surface area and even comparatively lower cost for water treatment. Some of these goals have been achieved by the calcination of kaolinite clays with pulverized *Carica papaya* seeds [31]. However, some clay properties suggest that not all such synergistic combinations may yield composites of better adsorption efficiencies. Hence, the aim of the study was to determine if calcined bentonite-biomass composites would yield higher adsorption efficiencies than the pristine bentonite clay. With the forgoing in mind, calcination of bentonite clay with pulverized *C. papaya* and pine cone were carried out in order to ascertain the above. The biomass-modified sorbents obtained were tested for the removal of Pb(II), Cu(II) and Cd(II) ions from aqueous solutions.

2. Materials and method

2.1. Materials and pretreatments of the sorbents

All reagents used for this study were analytical grade. Pb(II), Cd(II) and Cu(II) solutions were prepared from their chloride salts (Merck): lead (II) chloride (PbCl₂), cadmium (II) chloride (CdCl₂), copper (II) chloride (CuCl₂).

The *C. papaya* seeds were sourced from local markets in Ibadan, Nigeria. The pine cone seeds were obtained from the University of Ibadan, Botanical garden. The pretreatments and composites preparations were carried out by slight modification of the method of Unuabonah et al. [31]. All seeds were washed with tap water to remove dirt. These were sun-dried initially and later oven dried to remove moisture. The seeds were then pulverized to fineness using

a steel blender sieved through a 230 μm mesh size sieve and stored in an air-tight container.

Bentonite clay was obtained from the clay reserve of Federal Institute of Industrial Research Oshodi (FIRO), Lagos, Nigeria. The clay was pretreated by suspension in deionized water for 24 h in order to remove sand and heavy non-clay materials, and the suspension was carefully decanted to obtain the bentonite clay only. The clay was further treated to remove organic matter by adding 30% hydrogen peroxide solution and stirring the mixture until effervescence ceased. The mixture was decanted gently and washed five times to remove all traces of hydrogen peroxide and then oven dried at 105 °C until constant weight. After cooling, the clay was ground, sieved through a 230 μm mesh size sieve and stored in an air-tight container.

2.2. Preparation of biomass-modified clay adsorbent

Equal masses of purified bentonite and either of *C. papaya* or pine cone seeds (50 g each) were weighed into a 1 L beaker containing 300 mL of 0.1 M NaOH solution. The content was thoroughly stirred and heated in an oven at 105 °C until dryness. These samples were placed in separate crucibles and calcined at 300 °C for 6 h. The resultant dark powdery material was washed several times to remove residual NaOH and then oven dried at 105 °C. The pure bentonite, the *C. papaya* and pine cone seeds modified bentonite clay was referred to as BEN, CPB and PCB, respectively. Schematics of the modification processes are shown in Supporting material (SM) Fig. 1.

2.3. Characterization of the sorbents

The samples diffractogram were obtained with a Bruker phaser diffractometer system using the randomly oriented mounts procedure and scanning from 5 to 70°θ. pH of the samples were determined in deionized water (sample:water ratio of 1:2). The pH at point of zero charge (pH_{PZC}) was determined (SM 1) by the pH drift method [12]. Cation exchange capacity (CEC) of the

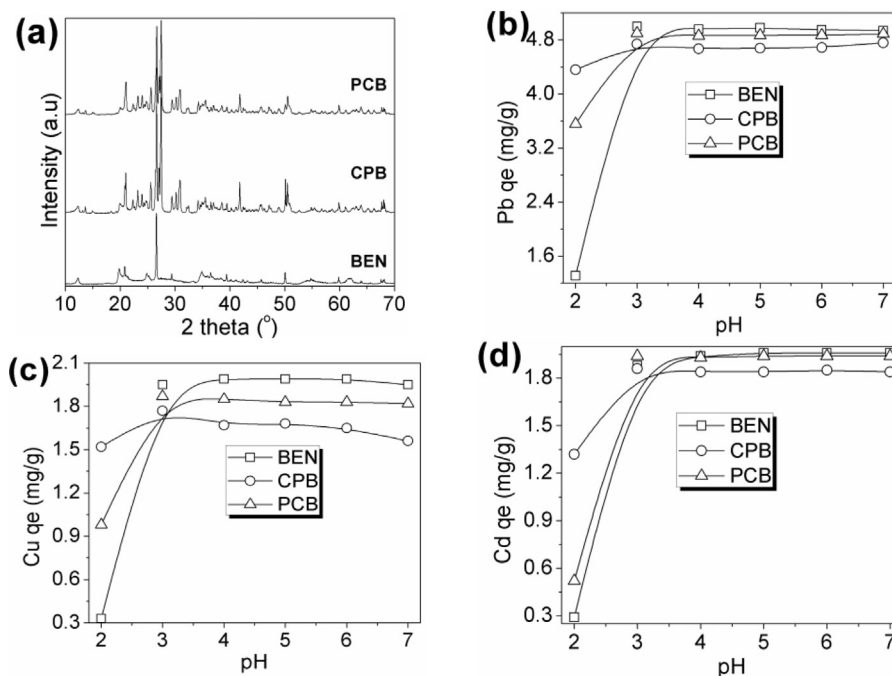


Fig. 1. (a) X-ray diffraction patterns of BEN, CPB and PCB; effect of pH on the adsorption of (b) Pb(II), (c) Cu(II) and (d) Cd(II) ions.

adsorbents was determined using the sodium saturation method by adding 25 mL of 1 M sodium acetate solution to 1 g of the adsorbent which resulted in the exchange of matrix cations with the added sodium ions. The samples were then washed with 15 and 10 mL portions of isopropyl alcohol to remove excess sodium acetate. The exchanged sodium ions on the adsorbents were subsequently washed with 15 and 10 mL portions of 1 M ammonium acetate solutions to displace the adsorbed sodium with ammonium. The concentrations of displaced sodium were determined. Surface area was determined using Micromeritics ASAP 2020 M + C accelerated surface area analyzer (Micromeritics Instrument Corporation, USA).

2.4. Micro-pollutants adsorption experiments

Adsorption experiments were carried out by adding 20 mL solution of specified concentration of the micro-pollutants (Pb(II), Cu(II) and Cd(II)) into vials containing 100 mg of the adsorbent. The adsorbent and micro-pollutant mixtures were then equilibrated by shaking at 100 rpm in a temperature (25 °C) controlled shaker until equilibrium; where necessary during the experiments, the pH of the working solutions were adjusted by adding drops of either HCl or NaOH. Effect of pH on adsorption of the micro-pollutants was carried out by varying pH from 2 to 7 using 50 mg/L of micro-pollutants and equilibrating for 1440 min, effect of time was investigated by using 50 mg/L of the micropollutant and time varied from 15 to 1440 min, equilibrium experiments were studied at temperatures of 25 and 50 °C, while varying the concentrations from 0 to 70 mg/L at solution pH of 5.0 ± 0.2 and equilibrating for 1440 min. At equilibrium, the vials were centrifuged at 3000 rpm for 10 min, and the concentrations of micro-pollutants left in solution were determined using the Varian AA240FS Atomic Absorption Spectrometer (AAS) with air-acetylene flame on absorbance mode. The experiments were conducted in duplicate and the mean of the values were used for computation.

2.5. Data treatment

The amounts of metal ions adsorbed were calculated from the initial (C_0) and final (C_e) concentrations in solutions after equilibration using Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where q_e , V and M are the amount of metal ions adsorbed (mg/g), volume of the solution (mL) and mass (g) of adsorbent used, respectively.

The linear forms of Lagergren [32] Pseudo-first order (PFO), Pseudo-second order (PSO) and the Weber and Morris [33] Intra-particle diffusion (IPD) models were used to describe the

adsorption data; as well as the Langmuir [34] and Freundlich [35] adsorption isotherm models (SM 2).

3. Results and discussion

3.1. Characterization Results

The powder XRD diffraction patterns (Fig. 1a) of BEN and the modified bentonite clays (CPB and PCB) revealed that the calcination of the clay did not lead to any observable change in the position of the diffraction peaks of all the adsorbents from 10 to $70^\circ 2\theta$ (0 0 1). The diffraction patterns of the modified clays were typically the same as those of the unmodified clays. This similarity between the diffractograms is an indication that biomass-modification of clays does not promote any structural modification in the basic d-spacing on the lattice structure of the pure clay mineral, except the impregnation of the calcined biomaterials on the clay surface. Similar result has been reported by Unuabonah et al. [31] for the biomass-modification of Kaolinite clay.

The XRD results were supported by other physicochemical parameters e.g. the specific surface area data showed that calcination of clays in the presence of biomass reduced the surface area of the clay (SM Table 1). The surface area of the clay reduced from $64 \text{ m}^2/\text{g}$ to ≈ 15 and $14 \text{ m}^2/\text{g}$ in the CPB and PCB adsorbents, respectively; the CEC reduced from 101.2 to 62.9 and 97.7 meq/100 g while the pH_{pzc} also reduced from 8.1 to 7.8 and 7.2 for CPB and PCB, respectively. The reductions in CEC and pH_{pzc} may be attributed to the slight chemical deformation of bentonite (dehydroxylation) caused by heating which does not affect the crystal structure [36].

3.2. Effect of pH on Pb(II), Cu(II) and Cd(II) adsorption

Fig. 1b and c shows the results of the effect of pH on the adsorption of Pb(II), Cu(II) and Cd(II) on BEN, CPB and PCB adsorbents. It was observed that the adsorption was pH dependent and increased with increase in pH until pH 3 where optimum adsorption were observed for all adsorbents. Similar adsorption trend has been reported in literature [12]. The quantities of metals ions adsorbed onto the clay adsorption sites were low at low pH values (less than 3), but as solution pH increased the quantities increased rapidly until optimum pH where the highest adsorption were recorded. These results showed that pure and modified bentonite clays can be used for adsorption of metals in solutions having pH between 3 and 7. This is a wide pH range of adsorption unlike those of most adsorbents in literature with narrow optimum pH range of adsorption; hence, these adsorbents may be applied for pollutants adsorption from a wide range of aqueous acidic solutions. This adsorption trend has been attributed to the nature and ionization of adsorption surfaces and metals ions in

Table 1
Calculated kinetics model parameters.

		BEN			CPB			PCB		
		Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)
PFO	q_e (mg g ⁻¹)	8.22	1.90	2.18	4.01	2.29	2.22	7.76	2.32	2.37
	$K_1 \times 10^{-4}$ (min ⁻¹)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	r^2	0.686	0.916	0.694	0.616	0.567	0.547	0.432	0.570	0.481
PSO	q_e (mg g ⁻¹)	0.49	0.10	0.15	0.43	0.19	0.18	0.49	0.19	0.19
	K_2 (g mg ⁻¹ min ⁻¹)	0.90	0.27	1.11	0.16	0.61	0.49	0.97	0.93	1.47
	r^2	1.000	0.996	0.999	0.999	0.999	0.999	1.000	1.000	1.000
IPD	C (mg g ⁻¹)	0.47	0.07	0.14	0.32	0.16	0.14	0.46	0.16	0.17
	K_{id}	0.007	0.001	0.001	0.003	0.001	0.001	0.001	0.001	0.001
	r^2	0.877	0.945	0.887	0.787	0.781	0.743	0.603	0.781	0.69
Experimental	q_e (μg g ⁻¹)	0.49	0.10	0.15	0.43	0.19	0.18	0.49	0.19	0.19

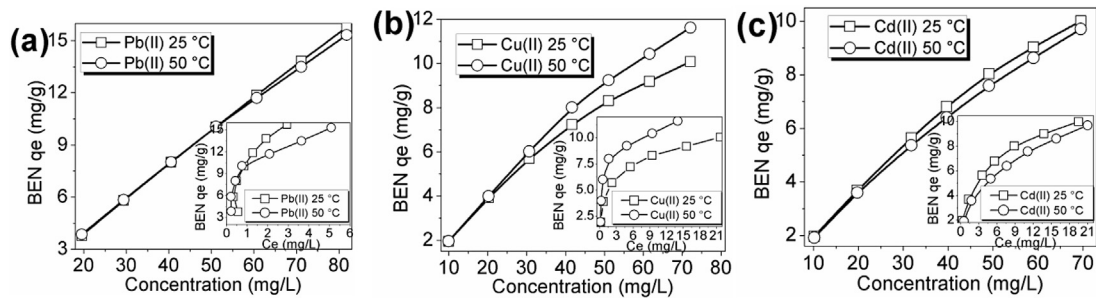


Fig. 2. Pure bentonite adsorption trend with increase in concentration for (a) Pb(II), (b) Cu(II) and (c) Cd(II) (Insert: isotherm plot of q_e vs C_e).

solution at various pH values [12]. At low pH values (around 2) there is stiff competition between the H^+ and positively charged metal ions for the negatively charged adsorption sites causing protonation of negatively charged adsorption sites, i.e. the sites become uncharged. This means that the metal ions may not have the opportunity of being adsorbed or are displaced from the adsorption sites by protons, both cases resulting in low surface adsorption. However, as solution pH increases, this competition reduces due to reduction in the concentration of H^+ in solution; resulting in increased adsorption. This increase in adsorption occurs steadily with pH until optimum pH when further adsorption is not possible and the horizontal part of the curve in Fig. 1 is observed.

The slight changes in pH_{pzc} (<1.0) from BEN to CPB and PCB notwithstanding (SM Table 1), it was observed that adsorption of these cations was significantly below the pH_{pzc} value. It has been suggested [31,37] that the modification process resulted in the formation of surface amide II groups (SM Fig. 2) whose delocalized π -electrons increased the electrostatic interactions between the adsorbents' surfaces and metal ions. The delocalized π -electrons were activated via calcination of the biomass materials. Hence, the cation adsorption may be attributed to electron donor–acceptor complexes in lewis bases of functional groups such as pyrones or chromenes [37].

3.3. Effect of time on Pb(II), Cu(II) and Cd(II) adsorption

The effect of time on the adsorption of Pb(II), Cu(II) and Cd(II) ions on BEN, CPB and PCB adsorbents (SM Fig. 3) suggested that the times for attainment of equilibrium for each metal differ from one sorbent to the other. For Pb(II) adsorption, equilibrium was attained in 400 min on BEN and PCB adsorbents, while the time was longer on CPB adsorbents. Cu(II) adsorption on BEN was very slow (1400 min) but it was faster in the modified adsorbents (400 min). However, Cd(II) adsorption showed similar trend for BEN, CPB and PCB adsorbents, and equilibrium was attained in approximately 500 min.

The effect of time data for the adsorption of Pb(II), Cu(II) and Cd(II) ions on BEN, CPB and PCB adsorbents were fitted to the PFO, PSO and IPD kinetics models. The estimated kinetics model parameters are shown in Table 1. It was observed that the PSO was more appropriate in describing the data than the PFO; comparison of the calculated PFO and PSO models parameters—adsorption capacity (q_e) and the magnitude of the correlation coefficient (r^2) values, showed that the PSO q_e values were closer to the experimental values and the r^2 values were closer to unity (≥ 0.996). The q_e values for the PFO showed very high overestimations of the adsorption capacities of the adsorbents and the r^2 values were not correlated. These results indicated that the

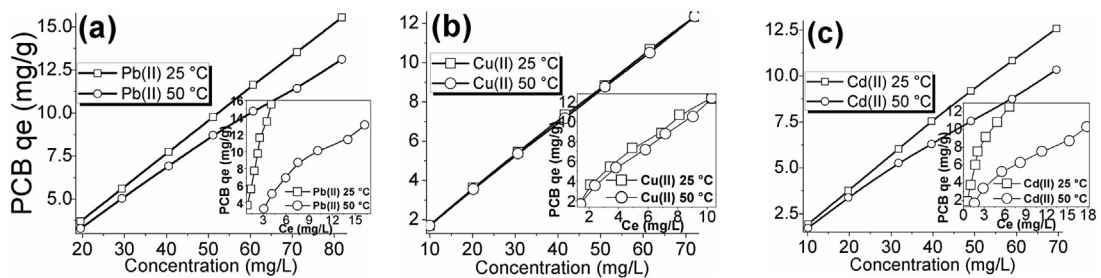


Fig. 3. PCB adsorption trend with increase in concentration for (a) Pb(II), (b) Cu(II) and (c) Cd(II) (Insert: isotherm plot of q_e vs C_e).

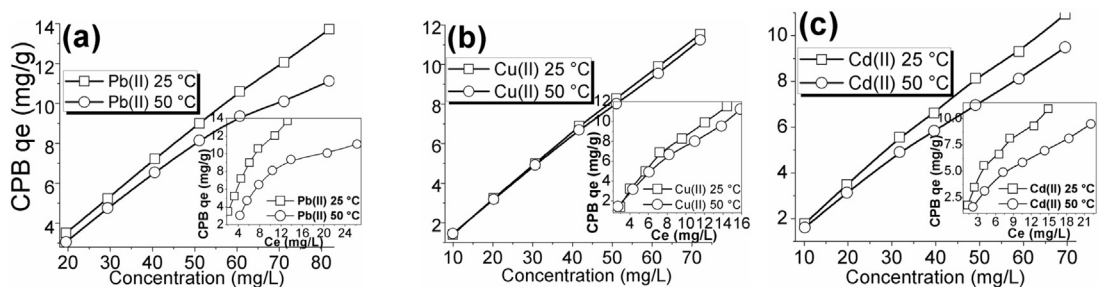


Fig. 4. CPB adsorption trend with increase in concentration for (a) Pb(II), (b) Cu(II) and (c) Cd(II) (Insert: isotherm plot of q_e vs C_e).

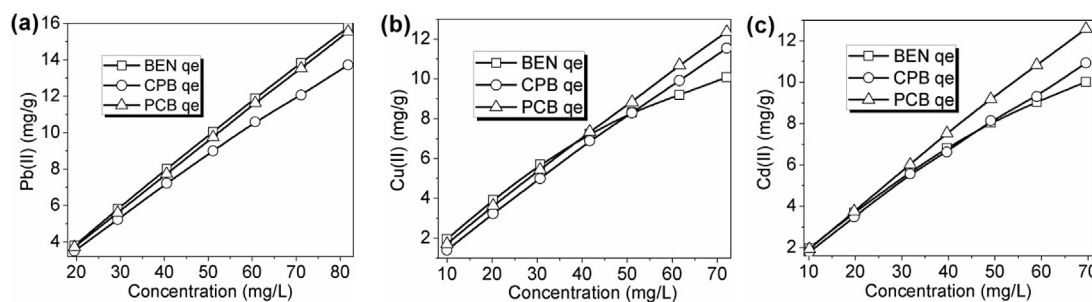


Fig. 5. Comparison of the adsorption trends of BEN, CPB and PCB with increase in concentration at 25 °C for (a) Pb(II), (b) Cu(II) and (c) Cd(II).

mechanism of removal of these metal species from aqueous solutions onto the adsorbents was ion exchange [12,14]. The values of IPD model parameter, C (mg/g) and r^2 values also showed that the data could be explained by this model. The magnitude of the parameter C indicated the thickness of the adsorbed species on the adsorbent surface; if the C value equals the experimental q_e values, then surface adsorption accounted for the bulk of the pollutants removal from solution [33]. In this study, it was observed that the bulk of the adsorption occurred on the surfaces of the adsorbents because the C (mg/g) values were approximately equal to the experimental q_e (mg/g) values (Table 1).

3.4. Equilibrium experiments and effect of temperature

Figs. 2–4 showed equilibrium adsorption trend as concentration increased. It was observed that increasing the concentration of the metal in solution resulted in higher sorption of the metal. This trend was attributed to the fact that when the transport of metals between the sorbent's external surface film and internal pores are equal, the trans-boundary movement of metals will not be significantly permissible; however, increasing concentration will re-initiate the trans-boundary movement and hence, the process will be concentration dependent. Similar findings have been reported in literature for similar and other pollutants adsorption [1,38,39]. The Figures also showed that increase in temperature did not lead to any significant increase in adsorption except for Cu(II) on the BEN clay.

The adsorption isotherm curves for all adsorbates obtained by plotting the q_e vs C_e data are shown in the inserts of Figs. 2–4. It was observed that the isotherm curves at both temperatures (298 and 323 K) fitted the L -type isotherm [40], and this was indicative of adsorbates adsorbed flat on the surface or sometimes, of vertically oriented adsorbates with particularly strong intermolecular attraction.

Comparing the adsorption of each metal by the BEN, CPB and PCB adsorbents—Fig. 5, it was observed that pine cone modification exhibited better adsorption capacity than the *C. papaya* modification and BEN for Cd(II) and Cu(II) adsorption while the adsorption of Pb(II) on all three adsorbents (Fig. 5b and c) showed that modification did not enhance the capacity of BEN for these

metals, instead a reduction was observed. It was also observed that increase in solution temperature resulted mainly in decrease in the uptake of the metal species from aqueous solution (Figs. 2–4).

The adsorption data at 298 K were fitted to the linear forms of the Langmuir and Freundlich adsorption isotherms (Table 2). It was observed that all data fitted the Freundlich adsorption isotherm model ($r^2 \geq 0.70$) with the exception of Cu(II) and Cd(II) adsorption on BEN which could be explained by both models. The Langmuir isotherm model assumes that the adsorption occur on sites having equal affinity for the pollutants and forms an adsorbate monolayer on the adsorbent surfaces at equilibrium. One reason Langmuir model could not be used to explain the data may not be unconnected to the fact that the adsorbents are composites having different adsorption sites being contributed by both the pure BEN and the calcined biosorbent material. However, the fitting of these results to the Freundlich isotherm model indicated that the adsorption occurred on heterogeneous surfaces of unequal energy with possible formation of adsorbate multilayer on the adsorbent surfaces at equilibrium. For the adsorption of Cu(II) and Cd(II) onto BEN which showed exceptions to the Freundlich isotherm model these were attributed to adsorption on different sites with similar energies. Such adsorption can easily be explained using the Langmuir isotherm model (Table 2). Also, combination of several Langmuir adsorption isotherm models occurring simultaneously have been shown to give a good approximation to the Freundlich type isotherm model [41]; hence, the data of Cu(II) and Cd(II) adsorption on BEN could be explained by both models. Pb(II) adsorption on BEN did not fit the Langmuir isotherm model, and this indicated Pb(II) adsorption occurred on heterogeneous surfaces of unequal energy.

In general, these biomass modifications of BEN did not enhance adsorption efficiency for the aqueous removal of Pb(II) but did for Cd(II) and Cu(II) ions. This may be explained thus: bentonite is a 2:1 expansive clay mineral and there is the likelihood that the modification blocked some pores on BEN while creating almost equal amount of new adsorption sites; secondly, Pb(II) [and to a lesser extent Cu(II)] form strong inner-sphere complexes with oxides of Fe, Al and Mn in clay minerals [42,43]; hence, blockage of the clay pores (reduction of access to oxides) may lead to reduced inner-sphere complex formation and consequently the reduced Pb

Table 2
Langmuir and Freundlich adsorption isotherm model parameters for Pb(II), Cu(II), and Cd(II) adsorptions.

Model	Parameter	Pb(II)			Cu(II)			Cd(II)		
		BEN	CPB	PCB	BEN	CPB	PCB	BEN	CPB	PCB
Langmuir	Q_0 (mg/g)	19.61	17.76	23.2	10.16	32.79	20	10.47	13.61	16.45
	β	1.15	0.19	0.35	0.84	0.03	0.13	0.52	0.19	0.41
	r^2	0.69	0.75	0.42	0.99	0.07	0.44	0.98	0.81	0.79
Freundlich	n	0.54	0.73	0.99	0.32	1.24	0.92	0.39	0.70	0.73
	K_f	9.36	2.26	4.10	4.02	2.01	1.58	3.30	1.77	3.69
	r^2	0.70	0.98	0.98	0.97	0.94	0.97	0.99	0.97	0.96
Experimental q_e (mg/g)		15.78	13.72	15.55	10.08	11.54	12.36	10.01	10.93	12.58

(II) adsorption. However, since Cd(II) and Cu(II) ions are retained by weaker exchange reactions in clay minerals [42], the new surfaces introduced by the modifications became adsorption sites for both cations, hence the slightly improved adsorption.

4. Conclusion

Synergistic combination of low-cost adsorbents is a promising technology for enhanced removal of aqueous pollutants from solution. However, not all composites of clay and biomass enhance aqueous metal removal efficiency as revealed in this study. The present study showed that modification of bentonite clay with *C. papaya* seeds or pine cone using the calcination method is possible but the process did not enhance the adsorption capacity of bentonite clay for the aqueous removal of Pb(II) but did for Cd(II) and Cu(II) ions. However, other parameters such as removal of adsorbent bleeding, easier separation of bentonite clay (high swelling clay) from aqueous solution and better mechanical strength were achieved. Another striking observation was that the adsorption efficiencies of these sorbents were stable over a wide range of pH (pH 3–7). Hence the modification process was successful and the modified adsorbents can reduce adsorbent bleeding, enhance separation of bentonite from aqueous solution, improve mechanical strength, as well as produce adsorbents that may be applied for pollutants removal from a wide range of aqueous acidic solutions.

Acknowledgements

We acknowledge the supports of Alexander von Humboldt Stiftung Foundation Research group linkage Program and the Institute of Soil Science and Soil Conservation, Justus Liebig University, Giessen, Germany where part of the study was done.

Appendix A. Supplementary data

Further information on the: SM Fig. 1—Schematic of bentonite modifications with Carica Papaya and Pine cone; SM 1: pH at point of zero charge (pH_{pzc}) determination; SM Table 1—Physicochemical parameters of the pure and modified bentonite clays; SM 2: Data Treatment; SM 3: FTIR Spectra; SM Fig. 2—Infra red spectra of BEN, CPB and PCB adsorbents; SM Fig. 3—Effect of time on the adsorption of (a) Pb(II), (b) Cu(II) and (c) Cd(II) ions on BEN, CPB and PCB adsorbents.

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jece.2016.01.044>.

References

- [1] B.I. Olu-Owolabi, P.N. Diagboya, K.O. Adebowale, Evaluation of pyrene sorption–desorption on tropical soils, *J. Environ. Manage.* 137 (2014) 1–9.
- [2] C.P. Okoli, G.O. Adewuyi, Q. Zhang, P.N. Diagboya, Q. Guo, Mechanism of dialkyl phthalates removal from aqueous solution using γ -cyclodextrin and starch based polyurethane polymer adsorbents, *Carbohydr. Polym.* 114 (2014) 440–449.
- [3] B.I. Olu-Owolabi, P.N. Diagboya, K.O. Adebowale, Sorption and desorption of fluorene on five tropical soils from different climates, *Geoderma* 239–240 (2015) 179–185.
- [4] S.R. Hejazi, J. Yadollahi, M. Shahverdi, J. Malakootikhah, Identifying nanotechnology-based entrepreneurial opportunities in line with water-related problems, *Middle East J. Sci. Res.* 8 (2011) 337–348.
- [5] K.G. Bhattacharyya, S.S. Gupta, Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review, *Adv. Colloid Interface Sci.* 140 (2008) 114–131.
- [6] M.A. Olivella, P. Jove, A. Oliveras, The use of cork waste as a biosorbent for persistent organic pollutants—study of adsorption/desorption of polycyclic aromatic hydrocarbons, *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* 46 (2011) 824–832.
- [7] B.I. Olu-Owolabi, P.N. Diagboya, W.C. Ebadan, Mechanism of Pb(II) removal from aqueous solution using a nonliving moss biomass, *Chem. Eng. J.* 195–196 (195) (2012) 270–.
- [8] S.W. Al Malli, A.A. Dahmani, M.M. Abuein, A.A. Gleza, Biosorption of mercury from aqueous solutions by powdered leaves of castor tree (*Ricinus communis* L.), *J. Hazard. Mater.* 152 (2008) 955–959.
- [9] B. Chen, M. Yuan, H. Liu, Removal of polycyclic aromatic hydrocarbons from aqueous solution using plant residue materials as a biosorbent, *J. Hazard. Mater.* 188 (2011) 436–442.
- [10] S.M. De Oliveira Brito, H.M. Andrade, L.F. Soares, R.P. De Azevedo, Brazil nut shells as a new biosorbent to remove methylene blue and indigo carmine from aqueous solutions, *J. Hazard. Mater.* 174 (2010) 84–92.
- [11] H.K. Hansen, F. Arancibia, C. Gutierrez, Adsorption of copper onto agriculture waste materials, *J. Hazard. Mater.* 180 (2010) 442–448.
- [12] A.E. Ofomaja, E.B. Naidoo, S.J. Modise, Removal of copper(II) from aqueous solution by pine and base modified pine cone powder as biosorbent, *J. Hazard. Mater.* 168 (2009) 909–917.
- [13] P. Saha, Assessment on the removal of methylene blue dye using tamarind fruit shell as biosorbent, *Water Air Soil Pollut.* 213 (2010) 287–299.
- [14] A. Seker, T. Shahwan, A.E. Eroglu, S. Yilmaz, Z. Demirel, M.C. Dalay, Equilibrium thermodynamic and kinetic studies for the biosorption of aqueous lead(II), cadmium(II) and nickel(II) ions on *Spirulina platensis*, *J. Hazard. Mater.* 154 (2008) 973–980.
- [15] R. Vimala, N. Das, Biosorption of cadmium (II) and lead (II) from aqueous solutions using mushrooms: a comparative study, *J. Hazard. Mater.* 168 (2009) 376–382.
- [16] P.N. Diagboya, B.I. Olu-Owolabi, K.O. Adebowale, Microscale scavenging of pentachlorophenol in water using amine and tripolyphosphate-grafted SBA-15 silica: batch and modeling studies, *J. Environ. Manage.* 146 (2014) 42–49.
- [17] P.N. Diagboya, B.I. Olu-Owolabi, D. Zhou, B.-H. Han, Graphene oxide–tripolyphosphate hybrid material: a potent sorbent for cationic dyes, *Carbon* 79 (2014) 174–182.
- [18] I. Ali, M. Asim, T.A. Khan, Low cost adsorbents for the removal of organic pollutants from wastewater, *J. Environ. Manage.* 113 (2012) 170–183.
- [19] I. Chaari, E. Fakhfakh, S. Chakroun, J. Bouzid, N. Boujelben, M. Feki, F. Rocha, F. Jamoussi, Lead removal from aqueous solutions by a Tunisian smectitic clay, *J. Hazard. Mater.* 156 (2008) 545–551.
- [20] L. Chen, S. Lu, Sorption and desorption of radiocobalt on montmorillonite—effects of pH, ionic strength and fulvic acid, *Appl. Radiat. Isot.* 66 (2008) 288–294.
- [21] E.F. Covelto, N. Alvarez, M.L. Andrade, F.A. Vega, P. Marcet, Zn adsorption by different fractions of Galician soils, *J. Colloid Interf. Sci.* 280 (2004) 343–349.
- [22] J. Hizal, R. Apak, Modeling of cadmium(II) adsorption on kaolinite-based clays in the absence and presence of humic acid, *Appl. Clay Sci.* 32 (2006) 232–244.
- [23] S.H. Lin, R.C. Hsiao, R.S. Juang, Removal of soluble organics from water by a hybrid process of clay adsorption and membrane filtration, *J. Hazard. Mater.* 135 (2006) 134–140.
- [24] J.C. Miranda-Trevino, C.A. Coles, Kaolinite properties, structure and influence of metal retention on pH, *Appl. Clay Sci.* 23 (2003) 133–139.
- [25] T.A. Elbokli, C. Detellier, Aluminosilicate nanohybrid materials. Intercalation of polystyrene in kaolinite, *J. Phys. Chem. Solids* 67 (2006) 950–955.
- [26] B. Zhang, Y. Li, X. Pan, X. Jia, X. Wang, Intercalation of acrylic acid and sodium acrylate into kaolinite and their in situ polymerization, *J. Phys. Chem. Solids* 68 (2007) 135–142.
- [27] M.F. Hou, C.X. Ma, W.D. Zhang, X.Y. Tang, Y.N. Fan, H.F. Wan, Removal of rhodamine B using iron-pillared bentonite, *J. Hazard. Mater.* 186 (2011) 1118–1123.
- [28] B. Sarkar, Y. Xi, M. Megharaj, G.S. Krishnamurti, R. Naidu, Synthesis and characterisation of novel organopolygorskites for removal of p-nitrophenol from aqueous solution: isothermal studies, *J. Colloid Interface Sci.* 350 (2010) 295–304.
- [29] B. Sarkar, Y. Xi, M. Megharaj, G.S. Krishnamurti, D. Rajarathnam, R. Naidu, Remediation of hexavalent chromium through adsorption by bentonite based Arquad(R) 2HT-75 organoclays, *J. Hazard. Mater.* 183 (2010) 87–97.
- [30] A.R. Kul, H. Koyuncu, Adsorption of Pb(II) ions from aqueous solution by native and activated bentonite: kinetic, equilibrium and thermodynamic study, *J. Hazard. Mater.* 179 (2010) 332–339.
- [31] E.I. Unuabonah, C. Gunter, J. Weber, S. Lubahn, A. Taubert, Hybrid clay a new highly efficient adsorbent for water treatment, *ACS Sustain. Chem. Eng.* 1 (2013) 966–973.
- [32] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens, Handlingar* 24 (1898) 1–39.
- [33] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solutions. *Journal of Sanitary Engineering Division, Am. Soc. Civil Eng.* 89 (1963) 31–60.
- [34] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [35] H.M.F. Freundlich, Über die adsorption in lösungen, *Zeitschrift für Physikalische Chemie* 57A (1906) 385–470.
- [36] Y. Sarikaya, M. Onal, B. Baran, T. Alendaroglu, The effect of thermal treatment on some of the physicochemical properties of a bentonite, *Clays Clay Miner.* 48 (2000) 557–562.
- [37] J. Rivera-Utrilla, M. Sanchez-Polo, Adsorption of Cr(III) on ozonised activated carbon. Importance of C π -cation interactions, *Water Res.* 37 (2003) 3335–3340.
- [38] C. An, G. Huang, H. Yu, J. Wei, W. Chen, G. Li, Effect of short-chain organic acids and pH on the behaviors of pyrene in soil–water system, *Chemosphere* 81 (2010) 1423–1429.
- [39] S.C.G. Teixeira, R.L. Ziollli, M.R.C. Marques, D.V. Pérez, Study of pyrene adsorption on two brazilian soils, *Water Air Soil Pollut.* 219 (2011) 297–301.

- [40] C.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids, *J. Soc. Dyers Colourists* 74 (1960) 3973–3993.
- [41] W.J. Weber Jr., P.M. McGinley, L.E. Katz, A distributed reactivity model for sorption by soils and sediments: 1. Conceptual basis and equilibrium assessments, *Environ. Sci. Technol.* 26 (1992) 1955–1962.
- [42] I. Heidmann, I. Christl, C. Leu, R. Kretzschmar, Competitive sorption of protons and metal cations onto kaolinite: experiments and modeling, *J. Colloid Interf. Sci.* 282 (2005) 270–282.
- [43] P.N. Diagboya, B.I. Olu-Owolabi, K.O. Adebawale, Effects of aging soil organic matter, and iron oxides on the relative retention of lead, cadmium, and copper on soils, *Environ. Sci. Pollut. Res.* 22 (2015) 10331–10339.