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PART 1:

Journal Name:	<u>American Chemical Science Journal</u>
Manuscript Number:	2013 ACSj 4299
Title of the Manuscript:	Equilibria and kinetic studies on the adsorption of Cadmium onto Cameroonian wetland clays
Type of the Article	Research paper

General guideline for Peer Review process is available in this link:

[\(http://www.sciencedomain.org/page.php?id=sdi-general-editorial-policy#Peer-Review-Guideline\)](http://www.sciencedomain.org/page.php?id=sdi-general-editorial-policy#Peer-Review-Guideline)

- This form has total 7 parts. Kindly note that you should use all the parts of this review form.



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PART 2: Review Comments

	Reviewer's comment	Author's comment (if agreed with reviewer, correct the manuscript and highlight that part in the manuscript. It is mandatory that authors should write his/her feedback here)
Compulsory REVISION comments	Persistent heavy metal ions in trace quantities are difficult to remove from aqueous solution.” Reference is needed. The original paper would be recommended for more details. What is metal ion concentration do authors mentioned? Technique for example reverse osmosis might be applied. “The process has the additional advantages of applicability at very low concentrations, suitable for both batch and continuous processes, ease of operation, little sludge generation, possibility of regeneration and reuse, and low capital cost (Mohanty et al., 2006; Zhu et al., 2008).” References are not appropriate. The references are about “Preparation and characterization of activated carbons from Sterculia alata nutshell by chemical activation with zinc chloride to remove phenol from wastewater” and “Retracted: Kinetic and isothermal studies of lead ion adsorption onto bentonite” but authors do not improve the statement above. The original paper would be recommended for more details. “Thus, adsorption is continuously becoming a	Krishna G. Bhattacharyya, Susmita Sen Gupta, 2007. Kaolinite and montmorillonite as adsorbents for Fe(III),Co(II) and Ni(II) in aqueous medium. Applied Clay Science 41, 1–9 More details are mentioned in the paper These references are replaced by these two ones: Yavuz, O., Altunkaynak, Y., Guzel, Y., 2003. Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. Water Res. 37, 948–952. Saleh Kaoser, Suzelle Barrigton, Maria Elektorowicz, Li Wang, 2005. Effet of Pb²⁺ and Cd²⁺ on Cu²⁺ by bentonite liners. Can.J civ. Eng. 32, 241-249.



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	preferred method for removal, recovery and recycling of toxic heavy metals from wastewaters.” This is not appropriate. Most other Techniques are also continuously becoming a preferred method for removal, recovery and recycling of toxic heavy metals from wastewaters. “Different types of adsorbents are used for removing metal ions from aqueous solutions (Mohan et al., 2001; Gupta et al., 2003; Chiron et al., 2003; Peric et al., 2004; Alvarez- Ayuso and Nugteren, 2005), each presenting some limitations that may include either cost of the materials or complex chemistry hindering recovery.” Give one reference for each type for adsorbent. All references do not included cost analysis how to have this statement? “Clay minerals are important constituents of soil and they play the role of a natural scavenger for metals as water flows over soils or penetrate underground.” Reference is needed. The original paper would be recommended for more details. “By clay standards, kaolinite (AL₂Si₃O₅(OH)₄, are the principal constituent of soil nanostructure (up to 40% minerals in sedimentary rocks), (Ndibewu et al., 2010; Pedra et al., 2007).”	Alvarez-Ayuso, E., Nugteren, H.W., (2005). Purification of chromium (VI) finishing wastewaters using calcined and uncalcined Mg–Al–CO₃–hydrotalcite. Water Res. 39, 2535–2542. Krishna G. Bhattacharyya, Susmita Sen Gupta, 2007. Kaolinite and montmorillonite as adsorbents for Fe(III),Co(II) and Ni(II) in aqueous medium. Applied Clay Science 41, 1–9
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	“The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), Brönsted and Lewis acidity, etc., have made the clay minerals excellent materials for adsorption (Tanabe., 1981).” Scientific research would be also recommended for more details. “Mellah and Chegrouche (1997) had used bentonite for removing Zn(II) from aqueous solution with Langmuir monolayer capacity of 52.91 mg g⁻¹ at 293 K.” This is not really related to “Equilibria and kinetic studies on the adsorption of Cadmium onto Cameroonian wetland clays”. In addition, Mellah and Chegrouche concluded “The maximum monomolecular capacity Q₀ according to the Langmuir model is 52.91 mg/g for an initial zinc concentration of 300 mg/L at 20°C.” that is not reasonable. “The adsorption of Cd (II), Cu (II) and Zn(II) on sepiolite has also been reported (Sanchez et al., 1999).” The original paper would be also recommended for more details. Levy, R. and Francis, C.W. (1976), Adsorption and desorption of cadmium by synthetic and natural organo-clay complexes. <i>Geoderma</i>, 15 (5),	
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	361-370. Farrah, H. and Pickering, W.F. (1977), Sorption of lead and cadmium species by clay-minerals. <i>Australian Journal of Chemistry</i>, 30 (7), 1417-1422. “Original and Na exchanged bentonites have been used for the removal of Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from aqueous solution (Alvarez-Ayuso and Garcia-Sanchez, 2003) with maximum adsorption capacity of up to 49.8, 24.2, 23.1, 30.0 and 26.2 mg g⁻¹, respectively.” Why this is necessary? Are the adsorption capacities of 49.8, 24.2, 23.1, 30.0 and 26.2 mg g⁻¹ the highest? Or any other reasons? “The removal of Cr (III), Cr (VI) and Ag(I) from water by bentonite has also been reported (Khan et al., 1995) where Cr(III)-bentonite and Ag(I)-bentonite interactions were found to be exothermic while Cr(VI)-bentonite interactions was endothermic.” Why this is needed in “Equilibria and kinetic studies on the adsorption of Cadmium onto Cameroonian wetland clays”? “Strawn et al. (2004) reported the adsorption of Cu (II) by smectites (montmorillonite and beidellite) as a function of ionic strength and pH.” Why this is needed in” Equilibria and kinetic	Adsorption capacity is the highest He is needed to prove that in general, natural wetland clays is an excellent adsorbents
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	studies on the adsorption of Cadmium onto Cameroonian wetland clays” “For this type of clay material, the cation exchange capacity (CEC) = 12.04 meq/100 g was considered (Weiss and Amstutz, 1966).” This is quotation error. There is nothing about the statement above in the reference. “The size of the clay particles obtained was < 2 µm.” The size of the clay particles should be between two meshes. “These clay particles were dispersed in water and heated at 75°C in the presence of a solution of sodium bicarbonate salts (1.0 M), citrate (0.3 M), and chloride (2.0 M). The purpose of this treatment was to eliminate inorganic and organic compounds, aluminium found in the interlayer spaces and various free cations.” How to find aluminium is in the interlayer spaces and various free cations? “Carbonates were removed by treatment with HCl (0.5 M) and chloride was eliminated after several washings.” How to know “carbonates” were removed?	some isomorphic substitutions in the tetrahedral layer, such as Al^{3+} for Si^{4+}, develop negatively charged adsorption sites able to electrostatically adsorb cations Equilibrium adsorption studies is the part of Materials and methods
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	“2.4. Equilibrium adsorption studies” “2.4. Equilibrium adsorption studies” is not accepted. There is nothing about “Materials and methods” in “2.4. Equilibrium adsorption studies” “The sorption equilibrium data of Cd²⁺ on clay was analyzed using Freundlich and Langmuir isotherm models (Foo and Hameed, 2011).” The original papers would be also recommended for more details. Langmuir, I. (1918), The adsorption of gases on plane surfaces of glass, mica and platinum. <i>Journal of the American Chemical Society</i>, 40 (9), 1361-1403. Freundlich, H.M.F. (1906), Über die adsorption in lösungen. <i>Zeitschrift für Physikalische Chemie</i>, 57A, 385-470. Where x/m and C_e are the equilibrium concentrations of Cd²⁺ in the adsorbed and liquid phases in mg/g. K_F and n are the Freundlich constants that are related to the sorption capacity and intensity, respectively.” What are units of x, m, C_e, K_F, and n? “The Langmuir sorption isotherm equation” Why is C_e/q_e vs. C_e but are not $1/q_e$ vs. $1/C_e$ or q_e/C_e vs. q_e?	x/m (mg/g), C_e (mg/L), m (g), K_f (mg/g) and n (without unit) C_e/q_e vs. C_e is one of the possibility to write Langmuir linear equation
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	“2.5. Kinetic studies” “2.5. Kinetic studies” is not accepted. There is nothing about “Materials and methods” in “2.5. Kinetic studies” “Kinetic adsorption data were analyzed following pseudo-first-order kinetic model (Lagergren,1998) (3):” This is citation error. The original and the most frequently cited papers would be recommended for more details. Lagergren, S. (1898), Zur theorie der sogenannten adsorption gelöster stoffe. <i>Kungliga Svenska Vetenskapsakademiens. Handlingar</i>, Band 24, No. 4, 1-39. Ho, Y.S. (2004), Citation review of Lagergren kinetic rate equation on adsorption reactions. <i>Scientometrics</i>, 59 (1), 171-177. “The slope and intercept of plot of $\log(q_e - q_t)$ versus t (Fig. 9) were used to determine the first-order rate constant k_1. In many cases, the first-order equation of Lagergren does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (Ho and McKay, 2000). Kinetic data were further treated with the pseudo-second-order kinetic model (Ho and Wang, 2004). The pseudo-second-order equation is also based on the sorption capacity of the solid phase. Contrary to the other	
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	model, it predicts the behaviour over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step. The differential equation is the following:” This paragraph is not necessary in “Materials and methods”. “The slope and intercept of plot of t/q_t versus t (Fig. 10) were used to calculate the secondorder rate constant k_2. It is more likely to predict the behaviour over the whole range of adsorption and is in agreement with the chemisorption mechanism being the rate controlling step (McKay, 2000).” This paragraph is not necessary in “Materials and methods”. There is no reference (McKay, 2000). “2.6. Adsorption mechanism” “2.6. Adsorption mechanism” is not accepted. There is nothing about “Materials and methods” in “2.6. Adsorption mechanism” “In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber and Morris’s intraparticle diffusion model (Weber and Morris., 1963), in which the rate of intraparticle diffusion is a function of $t^{1/2}$ and can be defined as follows:” This is not necessary in “Materials and methods”	
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	“Where r_p is particle radius, D_t is the effective diffusivity of solutes within the particle, and K_w intraparticle diffusion rate. k_w values can be obtained by linearizing the curve $q = f(t^{1/2})$. Such types of plots may present a multi-linearity, implying that the overall adsorption process may be controlled by one or more steps, such as film or external diffusion, intraparticle diffusion and a chemical reaction on the pore surface, or a combination of more than one step.(Weber and Morris,1963) reported that if intraparticle diffusion was involved in the adsorption process, then a plot of the square root of time versus the adsorption amount would result in a linear relationship, and that the intraparticle diffusion would be the controlling step if this line passes through the origin.” This is not necessary in “Materials and methods” “Fig. 9 shows the effect of contact time on removal of Cd^{2+}.” Figure 9 does not show what authors mentioned. Figures 5, 8, 9, and 10 are not necessary. They are from the same experimental data. A figure q_t vs. time with experimental data as points and kinetic models as curves is needed. “Experimental studies were carried out with varying initial metal ion concentrations of Cd^{2+}	The data of first and second order equation derive of the data of an effect of contact time on removal of Cd^{2+}. using filter paper
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	ranging from 10 – 60 ppm using 0.2 g of adsorbent.” How to separate adsorbent from? “Equilibrium adsorption was established within 30 min for the metal ion.” Why experimental data after 30 min are needed? Kinetic experimental design is not accepted. “This data is important because equilibrium time is one of the parameters for economic feasibility studies for in wastewater treatment plant application (Kadirvelu and Namasivayam, 2003).” Why experimental data after 30 min are needed? What are the reasons for economic feasibility studies. “According to these results, the agitation time was fixed at 2h for the rest of the batch experiments to make sure that equilibrium was attained.” Authors noticed that “Equilibrium adsorption was established within 30 min for the metal ion.” Why authors fixed agitation time to be 2 h? Why authors spend more cost on agitation? “The equilibrium experiment was studied at room temperature, adsorbent mass: 0.2g, C₀: 10 – 60 ppm.” This should not be in 3. Results and discussions	I spend more cost on agitation to make sure the equilibrium was established
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	but should be in 2. Materials and methods. What is room temperature? Room temperature would not be always the same. Authors also noticed that “Adsorption isotherms provide qualitative information on the nature of the solute – surface interaction, as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature.” Isotherm experimental design is not accepted. “In order to understand the adsorption mechanisms of Cd²⁺ onto the clay, two adsorption isotherm models, Langmuir and Freundlich, were used to fit the experimental data.” How to know adsorption mechanisms form isotherm? “For determining the isotherm parameters (Table 2) by using non-linear regression, Origin version 7.0, a window based statistical software, was used. Different adsorption isotherms obtained at clay are illustrated in Fig. 6 and 7.” Figures 6 and 7 are not necessary. They are from the same experimental data. A figure q_e vs. C_e with experimental data as points and isotherms as curves is needed. Why Figs. 6 and 7 are linear isotherms as authors noticed that “For determining the isotherm parameters (Table 2) by using non-linear regression, Origin version 7.0, a window	
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	based statistical software, was used.” “The values of the parameters and the correlation coefficients obtained at clay are listed in Table 2. It is well known that the Langmuir model is usually used with an ideal assumption of a monolayer adsorption surface (Langmuir, 1918). The value of correlation coefficients (R²) for the two models at different concentration shows that the goodness-of-fit of the models is Freundlich.” This is not accepted. Isotherm experimental design is not accepted. “The values of the parameters and the correlation coefficients obtained using non-linear regression by origin version 7.0 at four concentrations are listed in Table 3.” Why authors do not give non-linear pseudo-first-order model and pseudo-second-order model in this manuscript? “Adsorption equation obtained and the fitting of the kinetic models are illustrated in Fig.8-9. It was found that the fitting to Ho’s pseudo-second-order model gave the highest values of correlation coefficients more accurately than the other two models investigated. Therefore, Ho’s pseudo-second-order model could be used for the prediction of the kinetics of adsorption of Cd²⁺ on the activated carbon.”	
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	This is not accepted. Kinetic experimental design is not accepted. “The fittings of the experimental kinetic results to the two models are shown in Figs. 8-9 and the estimated parameters values are presented in Table 3. It can be seen from the R² values that the pseudo-second-order model gives the best fit (R²: 0.996–0.999) but its predicted q_e values are overestimated as compared to the experimentally observed values, especially at high cadmium concentration. However, q_e values estimated from the pseudo-second-order model are an extrapolation outside the time period that was experimentally investigated, the fact still remains that the model accurately predicts the adsorption kinetics throughout the period of experiments. Therefore, the pseudo-second-order model could be used for the prediction of the kinetics of adsorption of Cd²⁺ on clay. As for the other two models, it is not clear that there is a second best; Lagergren’s model performs reasonably well at high Cd²⁺ concentration and the goodness of fit deteriorates.” This is not accepted. Kinetic experimental design is not accepted. “Fig. 10 shows the intraparticle diffusion plot of the adsorption of Cd²⁺ on the clay at four concentrations.”	
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	Figures 5, 8, 9, and 10 are not necessary. They are from the same experimental data. A figure qt vs. time with experimental data as points and kinetic models as curves is needed. “As it can be seen from this figure (Fig. 10), the plots of clay show similar features that have two linear segments followed by a plateau. In the first 15 min, the first linear portion passed through the origin, implying that the intraparticle diffusion played an important role and controlled the rate of the adsorption. In the 60 min. that followed, the regression was nearly linear but did not pass through the origin, suggesting that the intraparticle diffusion was not the sole rate-controlling step in this stage. The Kw value evaluated from the first linear parts of these curves at 10, 20, 40 and 60 ppm was 0.106, 0.099, 0.088 and 0.028, respectively. The I-value decreased with the increasing concentration of Cd²⁺, which showed that the adsorption rate increased with the increasing concentration. Comparing to the plots of 10 ppm, 20 ppm, 40 ppm and 60 ppm, the plot of 60 ppm had an added curved portion in the first 5 min, showing that film diffusion played an important pole in this stage (Weber and Morris, 1963).” This is not accepted. Kinetic experimental design is not accepted.	
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	“The maximum adsorption for initial Cd²⁺ conc. (60 ppm) was found to be 13.869 mg/g of clay. The Langmuir and Freundlich isotherm equations were used to interpret the adsorption phenomenon of the adsorbate, and the Langmuir isotherm was found to best describe the experimental data.” This is not accepted. Isotherm experimental design is not accepted. “The kinetic rates were modelled using the Lagergren-firstorder and pseudo-second-order equations, and the pseudo-second-order equation was found to explain the adsorption kinetics most effectively. It was also found that the pore diffusion played an important role in the adsorption.” This is not accepted. Kinetic experimental design is not accepted. The manuscript is “Equilibria and kinetic studies on the adsorption of Cadmium onto Cameroonian wetland clays”. Authors presented 3.1. Characterisation of clay 3.2. Effects of contact time and initial concentration of Cd²⁺ 3.4. Equilibria isotherms 3.5. Kinetic studies 3.6. Adsorption mechanism There is no 3.3. In addition authors spend very limited spaces for equilibria isotherms and kinetic	
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	studies.	
<u>Minor</u> REVISION comments		
<u>Optional/General</u> comments		