

Single Component Adsorption of Nickel, Cadmium, Copper and Lead from Aqueous Solution Using Aswan Clay

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Abstract: *Metals discharged to wastewater pose a great threat to environment. Treatment for such metals contaminated wastewater is a must. Aswan clay (AC) was tested as adsorbent for the adsorption of Ni(II), Pb(II), Cd(II) and Cu(II) from aqueous solutions. Batch scale experiments were carried out to study the main adsorption parameters such as pH, adsorbent concentration, initial adsorbate concentration, and kinetics of biosorption. The aforementioned elements were removed using AC at a percentage of 94.05, 92.36, 92.83 and 97.41% for Cu (II), Cd(II), Ni(II) and Pb (II), respectively. The effectiveness of the studied biosorbent was demonstrated using wastewater samples emanating from electroplating shops and ceramic industry wastewater.*

Keywords: Aswan clay, adsorption, Freundlich and Langmuir

1. Introduction

Industrialization and urbanization have led to an increase in ecological problems. Water is particularly vulnerable to contamination from discharge of wastewaters by various industries. Nickel (II) and lead (II) appear in the waste streams of chemical manufacturing, electroplating, metal refining, textile, paints and pigment, fertilizers, ceramic, mining and metal finishing [1]-[5]. Cadmium (II) appears in water streams of smelting, metal plating industries, ferrochrome processing, ceramic, and acid main drainage [6]-[8]. Nickel (II) is considered as a suspect carcinogenic agent that may have a role in DNA transcription process causing important chromosomal aberrations [9]. Cadmium can cause a chronic health problems such as bone disease, lung diseases, liver damage and hyper tension [10]-[11] renal damage, chronic pulmonary problems [12]. Lead may affect the growth of children [13]. Copper can cause metabolic disorders; inhalation of copper produce symptoms similar to those of silicosis and allergic contact dermatitis. It may also cause hemolytic anemia and neurological abnormalities [14]-[15].

Removal of Pb (II), Ni(II), Cd(II) and Cu(II) from wastes is carried out using various techniques including precipitation with lime or sulfide, ion exchange, reverse osmosis, solvent extraction, membrane filtration and electrochemical treatment [16]-[17]. These methods suffer from high capital operational costs [18].

In developing countries, there is a pressing need to use available low cost materials for the treatment of wastes with simple working technology. In wastewater treatment, the process of the adsorption has an edge over other methods, due to its sludge free clean operation. Adsorption is classified as Best Available Technology Not Entailing Excessive Costs (BATNEEC) [19]. Adsorption of metals on activated carbon derived from different sources has been studied by some authors [20]; also carbon nanotubes were used to adsorb lead [21].

Natural clays are evaluated as an appropriate adsorbent due its low cost and high removal efficiency. Their sorption capabilities come from their high surface areas and exchange capacities. The negative charge on the structure of clay minerals gives the capability to attract metal ions [22]. Kaolinite and montmorillonite were used for removal of lead and cadmium and nickel [23]. In another study, removal efficiency of 52.91 mg/g was obtained for zinc removal using bentonite, another type of clay [24]. Vermiculite, a 2:1 clay mineral, was applied as adsorbent for removal of cadmium, zinc, manganese, and chromium from aqueous solutions. The quantity of adsorbed cations was 0.50, 0.52, 0.60, and 0.48 mmol g⁻¹ of Cd²⁺, Mn²⁺, Zn²⁺ and Cr³⁺ respectively [25]. Cu was adsorbed on natural and activated clays and the reported adsorption capacity was in the range of 9.2- 32.3 mg g⁻¹[26]. This work has attempted to utilize the Aswan clay as abundant inexpensive adsorbent for the removal of nickel, lead, cadmium and copper from aqueous solutions. Powdered AC was used in batch scale experiments for removing nickel (II), lead (II), cadmium (II) and copper (II) from aqueous solutions. The effects of pH, clay dose, initial metal concentration and contact time on adsorption efficiency were analyzed, and the optimum values were determined from the experimental studies. In order to determine the reaction of heavy metals with AC, experimental results were applied to Langmuir and Freundlich adsorption isotherms and the isotherm constants were obtained. Adsorption kinetics was applied in order to determine adsorption mechanism and adsorption characteristic constants. In addition, the evidence for physicochemical characteristics of Aswan clay obtained from X-ray diffraction (XRD) and scanning electron microscopy (SEM) were investigated to understand the adsorption mechanism.

2. Materials and methods

Clay analysis

X-ray diffractogram of a powdered sample was obtained using a (Type) X-ray diffractometer under operation conditions of 40.0 kV and 30.0 mA with Cu K α 1 radiation at

$\lambda = 1.54 \text{ \AA}$. The slit parameters used were: Divergence 1.00, scatter 1.00 and receiving 1.0 mm. The scanning parameters were: Axis $\theta - 2\theta$ ranging from 5.0 to 70.0, speed 4.00 min⁻¹, sampling pitch 0.080, and preset time of 0.40 s. Scanning electron microscopy studies were performed using a JEOL-JEM 1200 electron microscope operating at operated at an accelerating voltage of 20 KV. Prior to the observation, the surface of the samples was coated with a thin electric conductive gold film.

Adsorption experiments

All batch adsorption studies were carried out at ambient temperature ($25 \pm 5^\circ\text{C}$). 100 ml aliquot of the solution containing the desired quantities of Ni(II), Cd(II), Cu(II) and Pb(II) (as nitrates) were treated with 2 g of powdered AC for 24 h. The reaction mixture was filtered and the filtrate was analyzed for the remaining metal concentration using the Atomic Absorption Spectroscopy (AAS) [27]. The percentage of metal removal (R_e %) was calculated using the formula :

$$R_e \% = (1 - C/C_0) \times 100$$

Where C and C_0 are the final and initial concentrations of the ions in the test solution, respectively, while the adsorption capacity (mg/g) was calculated according

$$q = (C_0 - C)V/W$$

where V is the volume of solution and W represents the weight of the adsorbent used.

The effect of pH on the adsorption of Ni(II), Cd(II), Cu(II) and Pb(II) , onto AC was also studied individually using a 100 ml aliquot of a solution containing 5 mg l^{-1} of metal ion. 2.0 g of AC was added from each adsorbent separately and the pH was adjusted by adding either using 0.5 N HCl and 1N NaOH solutions (pH range was 3-9). Metal solution (5 mg l^{-1}) / sorbent mixture were left for 24 h, and then the amount of metal ion adsorbed was measured as mentioned before.

Adsorbate / adsorbent behavior was studied with Ni(II), Cd(II), Cu(II) and Pb(II). Solutions of concentration range of $1-7 \text{ mg l}^{-1}$ were used with the adsorbent dose concentration of 2.0 g/100 ml and left for 24 h at pH 6.4.

Sorbent dose optimization experiment was carried out by adding different weights of AC individually with a range of 0.5-3.0 g to 100 ml Ni (II), Cd (II), Cu (II) and Pb (II) solutions (5 mg l^{-1}) at the optimum pH and left for 24 h. The amount adsorbed of metal was calculated as mentioned above.

Kinetics of adsorption was also studied for AC over a time period of 40 hours with initial adsorbate concentration of 5 mg l^{-1} at the optimum pH. The residual quantity of Ni (II), Cd (II), Cu (II) and Pb (II) ions over the different contact time intervals was measured as mentioned before.

3. Results and Discussions

The results of the experimental studies carried out for the removal of heavy metals from synthetic wastewater samples using Aswan clay as an adsorbent are discussed below.

Effect of initial metal ion concentration

The effect of initial metal concentration on the removal percentage of heavy metals by AC is shown in Fig. (1). It can be seen that the percentage removal increases with the increase of metal concentration till optimum concentration then decreases with the increase of metal ion concentration.

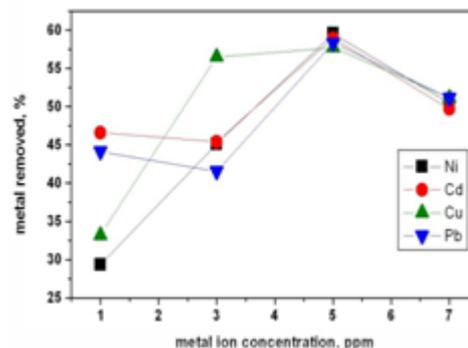


Figure 1: Effect of initial ion concentration

on the removal of Ni^{2+} , Cd^{2+} , Cu^{2+} and Pb^{2+} by Aswan clay. (clay dosage: 2g/100mL , pH 7, contact time 24h).

The percentage removal of heavy metals depends on the initial metal concentration. An adsorption peak was noticed at 5 ppm metal concentration which was almost for all ions used. The difference in percentage removals of different heavy metal ions attributed to the difference in their chemical affinity and ion exchange capacity with the respect to the chemical functional groups on the surface of the adsorbent. The optimum metal concentration was found to be as 5 mg l^{-1} .

Effect of adsorbent dose

The results obtained for removal of heavy metal ions with respect to the adsorbent dose are shown in Fig. (2). The percentage removal of heavy metal increases with the increase of adsorbent dose till it reached the maximum removal percentage at 20g l^{-1} of adsorbent (clay) dose for Ni (II), Cd (II) and Cu (II) ions, and above this an increase in solid content may hinder adsorption process; while for Pb (II) its removal percentage increases up to 30g l^{-1} of adsorbent dose. Thus, optimum clay dosage that can be used for almost all ions was 20g l^{-1} .

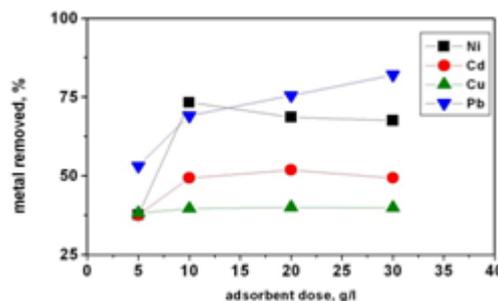


Figure 2: Effect of adsorbent dose on % removal of heavy metal ions

Effect of contact time

The effect of contact time on the adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) ions was investigated at different time

intervals in the range of 4–40 h using initial metal concentration of 5 mg l⁻¹ and adsorbent dose of 20 g l⁻¹. After they were centrifuged, the supernatant solutions were taken for metal ion analysis using AAS. As shown in Fig.(3), the adsorption equilibrium was established within 24 h, indicating that the initial adsorption was slow and the maximum uptake was reached within 24h for Pb (II), Cd (II) Ni (II) and Cu (II); thereafter, the amount of metal ion adsorbed almost remained constant.

This was due to the decrease of adsorption sites on the clay which gradually interacted with the metal ions, but the adsorption rate depends on the metal ions which transported from the bulk liquid phase to the actual adsorption sites on the surface of clay particles. Thus, the contact time of 24h was optimized and selected for the rest of the experiments. Also, it can be noticed that all of the tested metals has the same behavior with respect to contact time; while 56-65% removal was achieved within 24 hours for Ni, Cu, and Pb; only 50% for Cd.

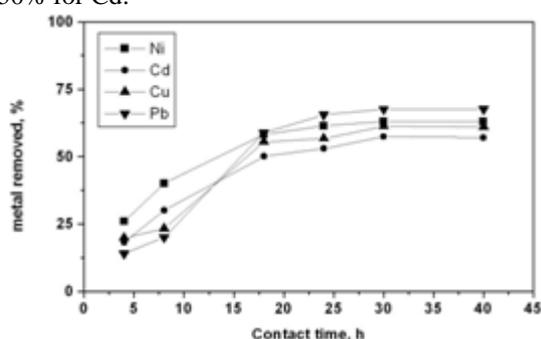


Figure 3: Effect of contact time on the amount adsorbed of Pb (II), Cd (II), Ni (II) and Cu (II) by the adsorbent at initial metal ion concentration: of 5 mg l⁻¹; dose of adsorbent: 20 g l⁻¹.

Effect of pH

pH is one of the most important parameters in controlling the extent of heavy metal ions uptake from their aqueous solutions. Fig. (4). shows the effect of pH on the percentage removal of heavy metal. The removal of metal is influenced by the pH. The maximum removal percentage of metal ion occurred at a pH of about 6.0.

It is assumed from the results of Fig. (4); that, at low initial concentrations, the predominant metal-retention mechanism is due to ion exchange, since at pH values lower than 6.0 (high acidity) the precipitation of metal is greatly limited [28]. At low pH values, where the concentration of H₃O⁺ is high, the competition by the active negative sites on the clay surface is enhanced and the metal sorption is reduced accordingly. With increasing pH, hydroxylation of the clay surface increased, and thus explains why the metal sorption was increased. The maximum removal percentage of Ni (II), Cd (II), Cu (II) and Pb (II) at pH 6 were found to be 94.05, 92.36, 92.83, 97.41%, respectively.

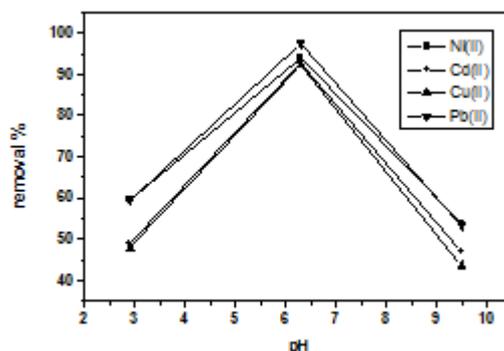


Figure 4: Effect of pH on metal ion adsorption

Sorption isotherms

Freundlich and Langmuir models are the simplest and most commonly used isotherms to simulate adsorption of components on to a solid from a liquid phase. The Langmuir model is valid for monolayer sorption on a surface containing a finite number of binding sites. It assumes uniform energies of sorption active sites on the surface of the solid and no transmigration sorbate in the plane of the surface. The Langmuir adsorption equation is written in the non-linear (curved) and linear forms as follows:

$$q_e = (Q_m b C_e) / (1 + b C_e) \text{ (non-linear form)}$$

$$1/q_e = 1/Q_m + 1/Q_m b C_e \text{ (linear form)}$$

Where Q_m is the maximum sorption capacity of the adsorbent (maximum quantity of metal ions per unit weight of clay to form a complete monolayer on the surface mg g⁻¹) and b is a constant related to the binding sites with the metal ions (sorbate, L mg⁻¹). The isotherm data has been linearized using the linear form of Langmuir equation and is plotted between $1/q_e$ versus $1/C_e$, where a straight line could be obtained with a slope of $1/Q_m b$ and an intercept of $1/Q_m$, from which the monolayer capacity Q_m and b constant can be calculated .

The Freundlich equation is an empirical adsorption model that can be expressed as

$$q_e = K C_e^{1/n}$$

where q_e and C_e are defined previously, K is a Freundlich's constant related to the sorption capacity, and $1/n$ is considered to be a relative indicator of adsorption intensity. The linear form of Freundlich equation is:

$$\log q_e = \log K + (1/n) \log C_e$$

Freundlich constants, K and n are obtained from the linear plot of $\log q_e$ versus $\log C_e$. Freundlich isotherm model is widely used but does not provide the information on the monolayer adsorption capacity. The least-square method has been used to fit the experimental data by Langmuir and Freundlich isotherms for every element individually. Characteristic parameters obtained by the Langmuir and Freundlich equations are presented in Table 1.

Table 1: Characteristic parameters obtained by the Langmuir and Freundlich equations, where R is the correlation coefficient

Metal	Langmuir			Freundlich		
	b	Q_m (mg/g)	R^2	$1/n$	K	R^2
Ni ²⁺	0.052	3.24	0.97	0.565	7.57	0.92

Cu ²⁺	0.055	2.91	0.93	0.617	7.674	0.90
Cd ²⁺	0.436	10.64	0.99	0.837	13.152	0.94
Pb ²⁺	0.324	9.00	0.98	0.935	11.72	0.92

It is clearly noticed that the high values of regression correlation coefficient, R², are obtained when the results fitted with Langmuir isotherm. This reveals that the nature of adsorption may be as homogeneous monolayer on the adsorbent. The Langmuir constant Q_m, which is a measure of the monolayer adsorption capacity of Aswan clay is obtained as 3.24, 2.91, 10.64 and 9.00 mg g⁻¹ for Ni(II), Cu(II), Cd(II) and Pb(II), respectively, at pH of 6.4. These values are comparable with the values obtained for these metal ions using Na-mentmorillonite [28].

Clay structure

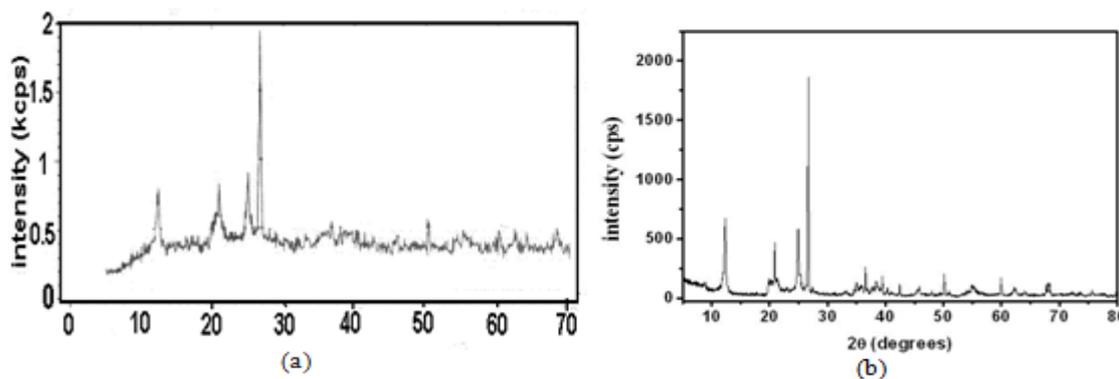


Figure 5: XRD diffractogram of Aswan clay before (a) and after (b) immersion in 5 ppm of Ni, Cu, Cd and Pb ions sample morphology. The SEM micrograph of the untreated AC sample is shown in Fig. (6).

In order to know the microstructure of AC, scanning electron microscopy (SEM) was generally employed to visualize

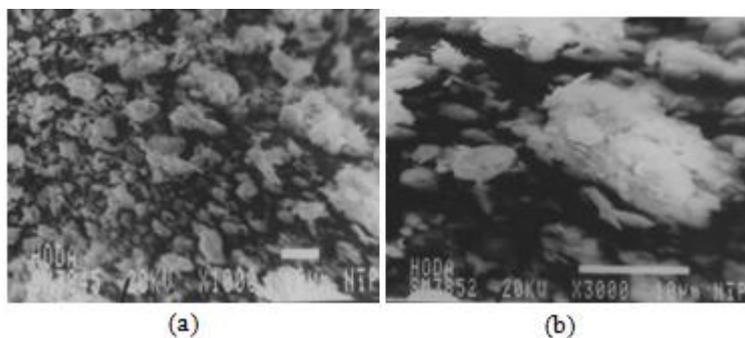


Figure 6: Scanning electron micrographs of Aswan clay at different magnifications : (a) X1000 and (b) X3000

It can be seen that, the particles are separated in the powder with varying sizes of the particles. Upon immersion of the clay in metal ion solution the surface modification is clear as shown in Fig. (7).

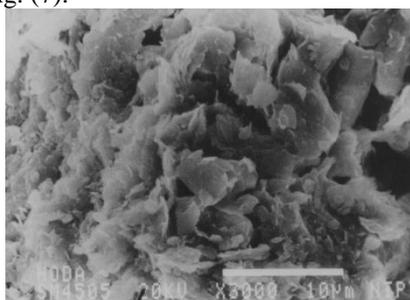


Figure 7: Scanning electron micrograph of Aswan clay after adsorption from solution of 5 ppm of Ni, Cu, Cd and Pb ions

The XRD diffractogram of the clay used in this study is fitted well with sandy soil clay (Fig. 5a). The chemical analysis of AC was found to be SiO₂ (65.9%), Fe₂O₃ (8.06%), Al₂O₃ (10.45%), ZnO (1.38%), MnO (0.95%), CaO (0.86%), and Na₂O (1.03%). XRD-diffractogram of AC gave 3 strong peaks at 2θ equal □ 20.915, 24.995 and 26.695^o with full width at half maximum of 1.345^o, 0.687^o and 0.416^o, respectively. These peaks support the chemical analysis that most of the sample composed of low quartz SiO₂.

The introduction of metal ion species in the interlayer space of the clay is not clear by comparing the XRD pattern of the bare clay with that of the clay immersed in 5 ppm of Ni, Cu, Pb and Cd ions (Fig 5b). The XRD pattern exhibited sharp peaks similar to that of the bare clay.

4. Conclusion

The removal of metal ions from waste stream using natural sorption technology was studied. Aswan clay (natural material) is an effective adsorbent for removal of Ni (II), Cd (II), Cu (II) and Pb (II) ions from synthetic wastewater. The removal percentage obtained using AC were 81.23, 79.97, 77.46 and 79.95 % for Ni (II), Cd (II), Cu (II) and Pb (II), respectively, with adsorbent dose 20 g l⁻¹.

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References

- [1] H. Parab, S. Joshi, N. Shenoy, A. Lali, U. S. Sarma, M. Sudersanan, Determination of kinetics and equilibrium of Co (II), Cr (II), Ni (II) onto coir pith, *Process Biochem.*, 41, pp. 60-90, 2006.
- [2] USDHHS, Toxicological profile for Zinc US Department of health and human Services, Agency for toxic substances and Disease Registry, Atlanta, GA, 1993.
- [3] N.T. Abdel-Ghani, M. Hefny, G. A. F. El-Chagbaby, Removal of Lead from aqueous solution using low cost abundantly available adsorbents, *Int. J. Environ. Sci. Tech.*, 4 (1) pp. 67-73, 2007.
- [4] C. M. Zvinowanda, J. O. Okonkwo, M. M. Sekhula, N. M. Agyei, R. Sadiku, Application of maize tassel for the removal of Pb, Se, Sr, U and V from borehole water contaminated with mine waste water in the presence of alkaline metals, *J. Hazard. Mater.*, 164 (2-3) pp. 884-891, 2009.
- [5] A. A. Abia, J. C. Igwe, Sorption kinetics and intraparticle diffusivities of Cd, Pb and Zn ions on maize cob, *Afr. J. Biotech.* 4 (6) pp. 509 – 512, 2005.
- [6] E. Álvarez-Ayuso, A. García-Sánchez, Removal of Cadmium from aqueous solutions by palygorskite, *J. Hazard. Mater.* 147(1-2) pp. 594 -600, 2007.
- [7] O. S. Amuda, A. A. Giwa, I. A. Bello, Removal of heavy metal from industrial waste water using modified activated coconut shell Carbon, *Biochem. Eng. J.*, 36 (2) pp. 174-181, 2007.
- [8] V. K. Gupta, D. Mohan, S. Sharma, K. T. Park, Removal of chromium (VI) from electroplating industry waste water using bassage fly ash – a sugar industry waste material, *The Environmentalist*, 19 (2) pp. 129-136, 1999.
- [9] IARC, International Agency for Research on Cancer International Agency for Research on Cancer Monographs on the Evaluation of the Carcinogenic Risks to Humans, 49, "Chromium, Nickel and Welding " IARC publications 1990.
- [10] G. F. Nordberg, Health hazards of environmental Cadmium pollution, *Ambio*, 3, pp. 51-65, 1974.
- [11] R. Nath, R. Prasad, V. K. Palinal, R. K. Chopra, Molecular basis of Cadmium toxicity, *Prog. Food Nutr. Sci.* 8, pp. 109-163, 1984.
- [12] D. Mohan, S. Chander, Single component and multicomponent adsorption of metal ions by activated Carbons, *Colloid. Surf.*, A: 177, pp. 183-196, 2002.
- [13] A. Kafourous, G. Touloumi, V. Makropoulos, A. Loutradi, A. Papanagiotou, A. Hatzakis, Effects of lead on the somatic growth of children, *Arch. Environ. Health*, 52, pp. 377-383, 1997.
- [14] ATSDR (Agency for Toxic Substance and Disease Registry), Toxicological profile for Copper, Prepared by Syracuse Research corporation for ATSDR, U.S. Public Health Service under contract, 88- 0608- 2, 1990.
- [15] U. S. EPA Drinking water criteria document for copper prepared by the office of health and Environmental criteria and Assessment office. Cincinnati, OH, for the office of drinking water, Washington, DC, ECAO- CIN-417, 1987.
- [16] C. L. Lai, S. H. Lin, Electrocoagulation of chemical mechanical polishing (CMP) waste water from semi conductor Fabrication, *Chem. Eng.*, 95 (1-3) pp. 205-211, 2003.
- [17] A. H. Mahvi, Application of agricultural fibers in pollution removal from aqueous solution, *Int. J. Environ. Sci. Tech.*, 5(2), pp. 275-285, (2008).
- [18] N. Meunier, J. Laroulandie, J. F. Blais, R. D. Tygi, Cocoa shells for heavy metal removal from acidic solutions, *Bioresour. Technol.*, 90, pp. 255-263, 2003.
- [19] G. McKay, Use of adsorbents for the removal of pollutants from wastewaters, CRC press, 1995.
- [20] M. Kobya, Removal of Cr (VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies, *Bioresour. Technol.*, 91, pp. 317-321, 2004.
- [21] Y.-H. Li, Z. Di, J. Ding, D. Wu, Z. Luan, Y. Zhu, Adsorption thermodynamic, kinetic and desorption studied of Pb²⁺ on carbon nanotubes, *Water Research*, 39, 605-609, 2005.
- [22] S. Babel, T. A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, *Journal of Hazardous Materials*, 97 (1–3), pp. 219-243, 2003.
- [23] S. S. Gupta, K. G. Bhattacharyya, Immobilization of Pb (II), Cd (II) and Ni (II) ions on kaolinite and montmorillonite surfaces from aqueous medium, *Journal of Environmental Management*, 87 (1) pp. 46-58, 2008.
- [24] A. Mellah, S. Chegrouche, The removal of zinc from aqueous solution by natural bentonite, *Water Res.* 31, pp. 621–629, 1997.
- [25] M. G. da Fonseca, M. M. de Oliveira, L. N. H. Arakaki, Removal of cadmium, zinc, manganese and chromium cations from aqueous solution by a clay mineral *Journal of Hazardous Materials*, 137, pp. 288–292, 2006.
- [26] K. G. Bhattacharyya, S. S. Gupta, Removal of Cu (II) by natural and acid-activated clays: An insight of adsorption isotherm, kinetic and thermodynamics, *Desalination*, 272(1–3) pp. 66-75, 2011.
- [27] A. K. Meena, K. Kadirvelu, G. K. Mishra, Adsorptive removal of heavy metals from aqueous solution by treated sawdust (*Acacia Arabica*), *Journal of Hazardous Material*, 150, pp. 604-611, 2008.
- [28] C. F. Baes, E. R. Mesmer, *The Hydrolysis of Cations*, Wiley, New York, 1976.
- [29] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, Adsorption of heavy metals on Na-montmorillonite: effect of pH and organic substance, *Water Res.* 37, pp. 1619-1627, 2003.

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