THE STUDY OF THE REMOVAL CONDITIONS OF FREE CYANIDE FROM WASTEWATERS BY LAYERED DOUBLE HYDROXIDE THROUGH EXPERIMENTAL DESIGN TECHNIQUE, KINETIC AND EQUILIBRIUM STUDIES

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Abstract: In mining and metallurgical activities, wastewater must be treated before discharging into the environment because of high cyanide toxicity. One of the most effective technologies for cyanide removal is adsorption. In this research, layered double hydroxides (LDHs) known as anionic clays was synthesized by co-precipitation process using a 3:1 ratio of magnesium nitrate and aluminum nitrate and used for removal of cyanide from aqueous solutions. The chemical and mineralogical compositions of LDH were investigated using XRD, XRF, Scanning Electron Microscopy (SEM), and Wavelength Dispersive X-ray (WDX) analysis. Particle size of LDH was determined to be about 4 nm using Scherrer equation which indicates that the synthesized LDH is in the range of nano-sized materials. The effects of temperature, adsorbent dosage, stirring speed, and pH on the adsorption capacity of LDH for cyanide were investigated using experimental design method (DX7 software). Maximum adsorption capacity of synthesized LDH for cyanide was obtained about 73.80 mg/g at stirring speed of 500 rpm, 60ºC temperature, adsorbent weight of 1.5 g, and pH=9.52. The equilibrium and kinetic data were best fitted by Langmuir isotherm and pseudo-second order model, respectively. The adsorption rate limiting step was determined to be intra-particle diffusion based on Weber and Morris model. It was found that the adsorption of cyanide onto LDH was occurred through ion-exchange mechanism, due to the chemical composition and mineralogical structure of anionic clay. Moreover, LDH was synthesized using industrial grade salt, and the results showed that with an adsorbent dosage of 20 g/l, more than 84% of the cyanide can be removed from a real wastewater, and LDH has the potential for cyanide removal from aqueous solution.

Keywords: Cyanide contaminated wastewater, Layered Double Hydroxide, Adsorption, Design of experiments, Kinetic and equilibrium Modeling

1- INTRODUCTION

Cyanide is a very poisonous chemical compound and therefore, EPA has set an enforceable regulation for cyanide at 0.2 mg/l for industry wastewater. Nowadays, large volumes of wastewater are annually produced by various industrial activities such as mining (extraction of gold, silver, etc.), electroplating, and production of synthetic fibers, plastics, organic chemicals and pharmaceuticals. They usually contain high concentrations of either free or metal-cyanide complexes, and must be treated before releasing back into the environment (Khodadad et al. 2008, Lito, Aniceto, and Silva 2012). The main technologies for cyanide removal are electrowinning, acidification– volatilisation– reneutralisation, hydrolysis distillation, precipitation, oxidation of cyanate, flotation, reverse osmosis, alkaline-chlorination oxidation, electrodialysis, caro's acid, and biodegradation (Ojaghi et al. 2018). Adsorption is one of the most effective technologies for cyanide removal among other methods and has been widely used in many cases (Stavropoulos, Papadopoulou, and Papadimitriou 2016).

Anionic clays, normally named as LDH, are a part of natural or synthetic clays. LDH can be usually showed by the formula $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2][An^{-}_{x/n}.mH_2O]$, where M^{2+} is a divalent cation(such as Mg^{2+}, Co^{2+}, or Zn^{2+}), and M^{3+} is a three-valent cation (such as Al^{3+}, Ga^{3+}, Fe^{3+}, Mn^{3+} or Gd^{3+}), and A^{n-} denotes the interlayer anion (for example, NO^{3-} or Cl^{-}) which can balance the positive charges on the layers, and x is the $M^{3+}/(M^{2+} + M^{3+})$ molar ratio ($0.20 \leq x \leq 0.33$) (Lu et al. 2018). An excess positive charge is introduced in the octahedral layers as a result of isomorphic substitution of divalent cations by three-valent cations which is normally balanced by

exchangeable anions located in the inter laminar space. The positive charge would also be balanced by other anions in the solution, that is why LDH can be used as an anion exchanger (Hur and Reeder 2017). LDH has been largely used for removal of various anionic pollutants such as sulfate, arsenate, chromate, selenite, bromate, Antimonate, fluoride and phosphate due to its low-cost and simple preparation method, and also high sorption efficiency (Rahman et al. 2018).

In this research, LDH was synthesized using co-precipitation process by both analytical and industrial grade chemicals, and different analysis techniques were used to examine the chemical and mineralogical compositions. This study deals mainly with the optimization of the operating parameters affecting removal of free cyanide using experimental design method (DX7 software), and the real wastewater treatment. The kinetics was investigated, adsorption equilibrium was modeled, and the possible mechanism was proposed.

2- METHODS

2-1- Synthesis of Mg/Al LDH

A co-precipitation method was applied for synthesis. 0.75 mole Mg $(NO_3)_2 \cdot 6H_2O$ and 0.25 mole Al (NO3)3•9H2O were dissolved in 250 mL deionized water (solution A). Then, 2 moles NaOH was dissolved in 250 mL deionized water (solution B). Afterwards, B was added drop wise to A with a constant agitation rate at ambient temperature, and LDH was immediately formed as a white precipitate. The precipitate was washed and dried overnight at 80°C. Analytical grade reagents obtained from Merck Co., Germany.

The XRF and XRD analyses of LDH were performed using Philips PW1480, and X'Pert PRO Philips, respectively. SEM images were taken using a Philips XL30 SEM, and also WDX studies were carried out with a WDX 3PC, MICROSPEC Corp., USA. Crystallite dimensions were estimated with the Debye-Scherrer equation (Eq.1) (Sun et al. 2017).

$$D = {}^{\lambda K}/_{\beta\, Cos\theta} \quad (1)$$

2-2- Optimization of adsorption process

The effects of important parameters on cyanide removal was studied using experimental design method, Design-Expert Software v.7.1.5 (DX7.0). The number of experiments based on full factorial method was 16, and the factors and their levels were chosen as presented in Table 1.

All batch adsorption experiments were performed using 500 mL cyanide solution ([CN-]:265.7 ppm) and adequate amounts of Mg/Al LDH which were added to a 1-Liter Merck glass bottles and agitated for 48 h at a certain temperature. The concentration of CN- was analyzed with titration method at the end of the experiments. The equilibrium concentration (qe) and the concentration of cyanide at the time "t" were determined using Eq.2 and Eq.3.

$$q_e = {}^{(C_0 - C_e)V}/_{W} \quad (2)$$

$$q_t = {}^{(C_0 - C_t)V}/_{W} \quad (3)$$

Table 1. Effective factors and their levels for cyanide removal by LDH

Factors		Levels	
Symbols	Factors	low	High
T	Temperature (oC)	25	60
W	Adsorbent dosage (g)	0.8	1.5
R	Stirrer speed (rpm)	250	500

pH	pH	9.5	11

2-3- Equilibrium and kinetics studies

For equilibrium studies, different solutions with CN^- concentrations of 13.3, 26.6, 53.1, 79.7, 106.3, 159.4, 212.6, 265.7, 318.9, 372 and 425.2 mg/L were prepared. The pH values of solutions were pre-adjusted to 10 and they were agitated for 72h at ambient temperature. Kinetics studies were also carried out by adding 1 g LDH to 500 mL cyanide solution (CN^- Concentrations: 26.5, 106.3, 265.7, and 531.5 mg/L) at 100 rpm, 25℃ and pH=10 in a laboratory bottle roll. Some samples were taken at certain time intervals, and CN^- concentration was determined by titration.

3- FINDINGS AND ARGUMENT

3-1- Characterization of the synthesized LDH

The XRD spectra presented that the main peaks corresponded to the typical Mg/Al LDH. Based on the Scherrer equation, the size of LDH crystals was estimated to be 4.3361 nm which indicates that the synthesized LDH is a nano-adsorbent. Moreover, MgO (32%) Al_2O_3 (14%), Na_2O (4%) and L.O.I. (49%) were detected in LDH sample by XRF analysis, which was very similar to the chemical composition of anionic clays. SEM images also confirmed the structure of Mg/Al LDH.

3-2- Optimization of adsorption process

The effects of various parameters such as temperature, stirring speed, and dosage of adsorbent were investigated with some experiments designed by DX7. Temperature has a significant effect on cyanide uptake and qe value increased from 48 to 66.4 mg/L when temperature rises up to 60 °C (This represents the endothermic nature of cyanide adsorption on LDH). Increasing the agitation speed in the range of 250-500 rpm has improved the adsorption capacity due to the reduction in the thickness of Nernst diffusion layer, and consequently, the higher possibility of interactions between LDH and CN-. Also, more adsorption sites are available at higher amounts of adsorbent, which increases the capacity of adsorption from 55.13 to 59.30 mg/L, while the dosage of LDH changes form 0.8 g to 1.5 g (Hsu et al. 2007). The negative effect of pH on loading capacity may relate to the stability and structural changes of LDH, or an adsorption competition between OH- and CN- at a high pH level (pH> 9.5)(Yang et al. 2015). The effects of main and interaction parameters on cyanide adsorption was illustrated in Pareto Chart (Figure 2). It can be seen that the most significant parameters affecting cyanide removal in descending order of importance are temperature (A), agitation speed (C), dosage of adsorbent (B), and pH (D).

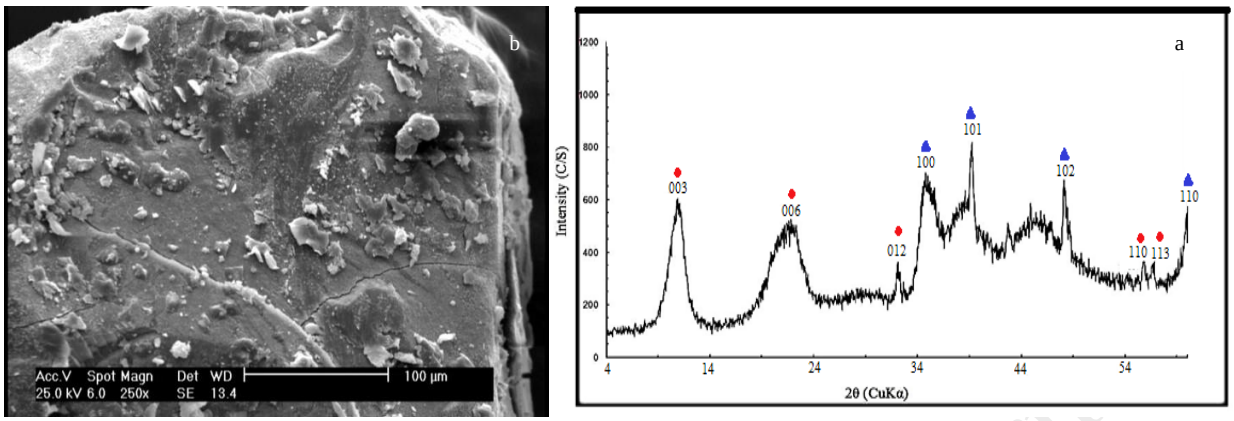

Figure 1. XRD spectra (a) and SEM image (b) of LDH

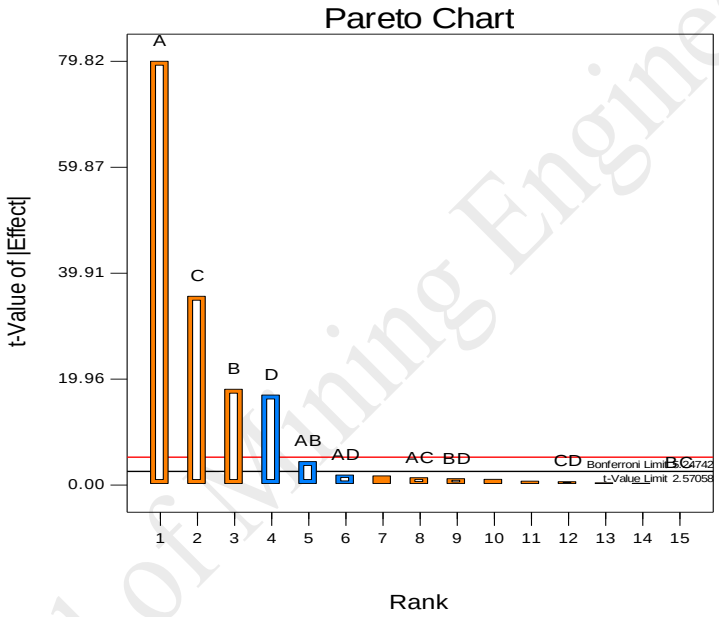

Figure 2. Pareto chart for effective parameters on cyanide removal by LDH

3-3- Kinetics and equilibrium studies

The equilibrium data for adsorption of CN^- with Mg/Al LDH were modeled with various isotherm models, including Langmuir and Freundlich. Correlation coefficient values (R^2) for both isotherm models were 0.985 and 0.956, respectively, which indicates that the equilibrium data was best fitted with Langmuir Isotherm.

Different kinetic models, such as Pseudo-First Order, Pseudo-Second Order, and Weber and Morris Intra-particle Diffusion Model were applied to study kinetics of free cyanide adsorption on Mg/Al LDH. Pseudo-Second Order model was determined to be the appropriate equation to estimate the kinetics of adsorption, because the model-predicted q_e value is quite similar to the experimental data (R^2=0.9796).

To assess the diffusion mechanism, Weber-Morris model was employed for intra-particle diffusion. Figure 3 represents the q_t versus $t^{0.5}$ plot for the cyanide concentrations of 26.5, 106.3, 265.7 and 531.5 mg/L. The plots consisted of two linear sections with different slopes which

shows that the intra-particle diffusion was not dominated in the whole adsorption process. The first step may relate to the cyanide diffusion onto LDH, and the second step may relate to the adsorption of CN^- on the adsorption sites. The mechanism of ion exchange between cyanide and intralayer onions maybe as the following equation:

$$Mg_{1-x}Al_x(OH)_2(NO_3)_x + xCN^- \rightarrow Mg_{1-x}Al_x(OH)_2(CN)_x + xNO_3^- \quad (4)$$

Activation energy was obtained to be about 6.4 $kJ.mol^{-1}$ using Arrhenius equation which confirms the physicochemical nature of the adsorption process. Maximum loading capacity (73 mg/g) was achieved at 60° C, 1.5 grams of adsorbent, 500 rpm agitation rate, and pH value of 9.52. Since the loading capacity of other common adsorbents for free cyanide is usually less than 10 mg/g (Eletta et al. 2016), recent results indicate that Mg/Al LDH would be a potential interesting adsorbent for cyanide removal. In addition, the LDH synthesized by industrial grade chemicals can adsorb 57mg/g free cyanide at the same condition, which is really considerable, thus it can be a good choice for CN^- removal due to the low-cost production process. The synthesized LDH was examined for the treatment of real cyanide contaminated wastewaters. In this case, 84% of cyanide was removed by LDH after 48 hours, and the loading capacity of 4.12 mg/g was reached, indicating that other anionic species of real solution was adsorbed on LDH along with cyanide.

4- CONCLUSIONS

Free cyanide removal from aqueous solution was investigated using Layered Double Hydroxide (LDH) which was synthesized with co-precipitation process using a 3:1 ratio of magnesium nitrate and aluminum nitrate.

Temperature had a significant effect on adsorption process, among other parameters such as agitation speed, dosage of adsorbent, pH, and their interactions.

The kinetics data was best fitted by pseudo second order model. Langmuir was appropriate to describe the adsorption of cyanide. Weber–Morris plots indicated that the adsorption of CN^- onto LDH had two-step and the rate-controlling step in the adsorption process might be related to intra-particle diffusion.

The activation energy was found to be 6.14 kJ/mol, which refers to the physicochemical sorption.

Industrial grade material was also used for synthesis and results showed that there was no big difference at the efficiency between LDH synthetized with analytical and industrial grade chemicals.

Treatment of a real cyanide contaminated wastewater was performed by low-cost LDH, and removal percentage was almost 84% which was significant.

Considering very fast adsorption kinetics, removing 70% of free cyanide at 30 min, and good efficiency, LDH proved be a novel and inexpensive adsorbent for the treatment of industrial effluent.

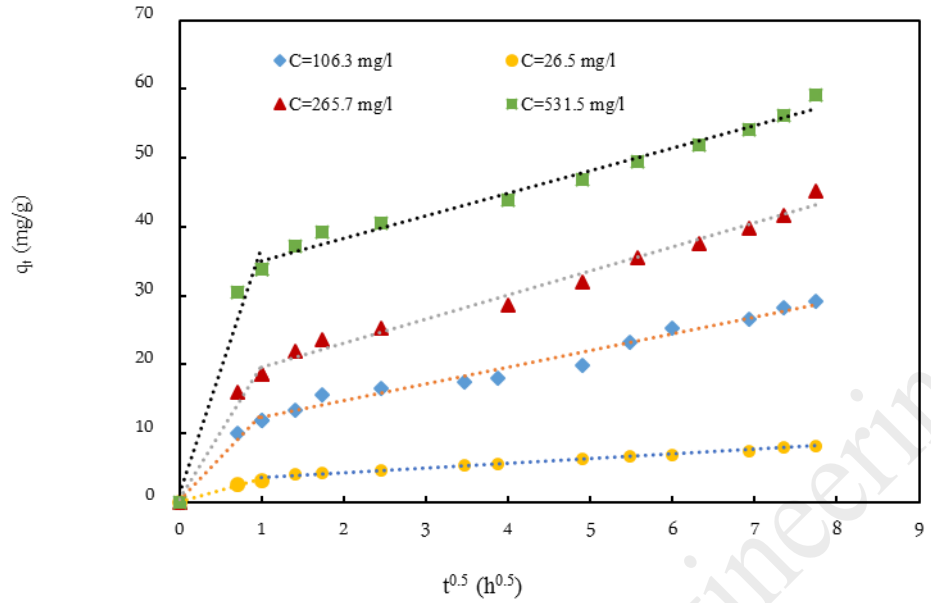

Figure 3. Intra- particle model for removal of cyanide by LDH at different concentrations

Refrences

- Eletta, O. A. A., O. A. Ajayi, O. O. Ogunleye, and I. C. Akpan. 2016. "Adsorption of cyanide from aqueous solution using calcinated eggshells: Equilibrium and optimisation studies." Journal of Environmental Chemical Engineering 4 (1):1367-1375. doi: https://doi.org/10.1016/j.jece.2016.01.020.
- Hsu, L. C., S. L. Wang, Y. M. Tzou, C. F. Lin, and J. H. Chen. 2007. "The removal and recovery of Cr(VI) by Li/Al layered double hydroxide (LDH)." J Hazard Mater 142 (1-2):242-9. doi: 10.1016/j.jhazmat.2006.08.024.
- Hur, Hyuck, and Richard J Reeder. 2017. "Formation of CoAl layered double hydroxide on the boehmite surface and its role in tungstate sorption." Journal of Environmental Sciences.
- Khodadad, A., P. Teimoury, M. Abdolahi, and A. Samiee. 2008. "Detoxification of Cyanide in a Gold Processing Plant Tailings Water Using Calcium and Sodium Hypochlorite." Mine Water and the Environment 27 (2):127-127. doi: 10.1007/s10230-008-0042-8.
- Lito, Patrícia F., José P. S. Aniceto, and Carlos M. Silva. 2012. "Removal of Anionic Pollutants from Waters and Wastewaters and Materials Perspective for Their Selective Sorption." Water, Air, & Soil Pollution 223 (9):6133-6155. doi: 10.1007/s11270-012-1346-7.
- Lu, Hongtao, Shuxia Liu, Hua Zhang, Yanling Qiu, Jianfu Zhao, and Zhiliang Zhu. 2018. "Decontamination of Arsenic in Actual Water Samples by Calcium Containing Layered Double Hydroxides from a Convenient Synthesis Method." Water 10 (9):1150.
- Ojaghi, Aghil, Sied Ziaedin Shafaie Tonkaboni, Parvin Shariati, and Faramarz Doulati

Ardejani. 2018. "Novel cyanide electro-biodegradation using Bacillus pumilus ATCC 7061 in aqueous solution." Journal of Environmental Health Science and Engineering 16 (2):99-108. doi: 10.1007/s40201-018-0289-3.

- Rahman, M. Tamzid, T. Kameda, S. Kumagai, and T. Yoshioka. 2018. "Effectiveness of Mg–Al-layered double hydroxide for heavy metal removal from mine wastewater and sludge volume reduction." International Journal of Environmental Science and Technology 15 (2):263-272. doi: 10.1007/s13762-017-1385-0.
- Stavropoulos, GG, M Papadopoulou, and K Papadimitriou. 2016. "A kinetic and thermodynamic study of cyanide adsorption in activated carbon." Desalination and Water Treatment 57 (46):21939-21943.
- Sun, Mingzhe, Ping Zhang, Daishe Wu, and Ray L Frost. 2017. "Novel approach to fabricate organo-LDH hybrid by the intercalation of sodium hexadecyl sulfate into tricalcium aluminate." Applied Clay Science 140:25-30.
- Yang, Qi, Yu Zhong, Xiaoming Li, Xin Li, Kun Luo, Xiuqiong Wu, Hongbo Chen, Yang Liu, and Guangming Zeng. 2015. "Adsorption-coupled reduction of bromate by Fe(II)–Al(III) layered double hydroxide in fixed-bed column: Experimental and breakthrough curves analysis." Journal of Industrial and Engineering Chemistry 28:54-59. doi: https://doi.org/10.1016/j.jiec.2015.01.022.