

Conservation of Reverse Osmosis Rejected Water Using Mg-Al-Layered Double Hydroxides As Adsorbents

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Abstract- In this study, Mg–Al–LDHs were prepared by the co-precipitation method and are calcined to get Mg–Al–Oxide. The structure, composition, morphology and thermal stability of the synthesized Mg–Al–oxides were analyzed by powder X-ray diffraction, SEM, Fourier transform infrared spectrometry and Thermogravimetry. Batch experiments were performed to study the absorption dissolved salts of RO rejected water as a function of pH, contact time, initial metal ion concentration, and adsorbent dose. Our results showed that Mg–Al–oxides can be used as an efficient adsorbent material for removal of dissolved salts from RO rejected water.

Keywords- RO rejected water, Layered double hydroxide.

I. INTRODUCTION

Hardness (hard water) is one of the common water quality problems throughout the world. A total of 70% of the earth's surface is covered by water. Of this, 97% is only sea water (non-drinkable). Only 2.5% of fresh water is accessible for human use and of this only 0.5% is used as drinking water. Hardness of water is caused as water picks up minerals such as magnesium and calcium ions from rocks and soil. Ground water contains more minerals than surface water, so it is harder than surface water. Hard Water is dangerous to health of human beings. It causes many diseases in humans. It also disturbs the industries due to the formation of scales and sludge in the boilers and coolant pipes. It is not safe to drink, also for other domestic purposes. Excess intake of calcium and magnesium can increase the risks of osteoporosis, nephrolithiasis, colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance and obesity. Hard water containing these ions can be treated at primary level for household purposes. Point-of-entry ion exchange (water softener) devices are used in some households to remove hardness (calcium, magnesium) and iron from water. Reverse osmosis (RO) systems are found to be the most convenient methods for the removal of dissolved salts from the water due to various advantages in the domestic side. This project is

aimed at the conservation of RO rejected water by treating with an adsorbent material like Layered Double Hydroxides (LDH) through a very simple process.

Layered double hydroxide (LDH) forms an important class of inorganic materials owing to their applications in the wide area of current research. Layered double hydroxides are obtained by partial isomorphous substitution of divalent metal ions by trivalent metal ions in the structure of mineral brucite, Mg(OH)₂. Chemical composition of a layered double hydroxide can be expressed by the general formula M^{II}_{1-x}M^{III}_x(OH)₂Aⁿ⁻_{x/n}yH₂O, where M^{II} and M^{III} are divalent and trivalent metal cations and Aⁿ⁻ is an n-valent anion. These compounds have a layered crystal structure composed of positively charged hydroxide layers of [M^{II}_{1-x}M^{III}_x(OH)₂]^{x+} and interlayers containing anions and water molecules. The value of x represents a portion of trivalent metal cations substituted in hydroxide layers and usually corresponds to 0.20 < x < 0.33.

The LDH anion exchange ability, large surface area and regeneration ability ensure that this adsorbent can be excellently utilized in wastewater purification (Roto et al.). Given that the calcination products of LDHs are mixed oxides, which are solids with basic properties (Sanchez-Valente et al.; Figueras et al.), LDHs and their oxides have been successfully employed as adsorbents for a variety of anion species and/or pollutants. LDHs can take up ionic species from solution by three different mechanisms: surface adsorption, interlayer anion exchange, and reconstruction of a calcined LDH by the 'memory effect' (Duan & Evans). LDHs have been successfully employed to remove heavy-metal ions from aqueous solution due to their high anion-exchange ability, high uptake capacity, large surface area, flexible interlayer space, ease of preparation, low cost, stability and regeneration ability, ensuring that this adsorbent can be excellently utilized in the treatment of RO rejected water. The effects of different adsorption parameters, such as solution pH, contact time,

initial metal concentration and adsorbent dose were studied for Mg–Al–LDH.

II. CHARACTERIZATION OF RO WATER

Sl. no.	Parameters	Units	Raw Water	Rejected Water
1	pH	-	7	7.2
2	Conductivity	mMhos/cm	0.890	1.065
3	Total alkalinity	mg/l	460	480
4	Total Dissolved Solids	mg/l	585	1080
5	Chlorides	mmol/l	52.48	162.9
6	Hardness			
	• Calcium	mg/l as CaCO ₃	268	491
	• Magnesium		317	589
7	Total hardness	mg/l as CaCO ₃	585	1080
8	Permanent hardness	mg/l as CaCO ₃	317	525
9	Temporary hardness	mg/l as CaCO ₃	268	555
10	Potassium	mg/l	8.4	19.2
11	Sodium	mg/l	45.6	75

III. SYNTHESIS OF LAYERED DOUBLE HYDROXIDES

Layered double hydroxides can be synthesized by urea hydrolysis, solid state reaction, co-precipitation, and hydrolysis of salts and oxides techniques.

Co-Precipitation Method

The co-precipitation technique is the most commonly used and simplest method. A solution containing the anion guest is added to an aqueous solution of two different metals that are used as precursors. This is followed by drop-wise addition of an alkaline solution to the mixture under vigorous stirring and a nitrogen atmosphere until a final pH of 7–10. The mixture is aged at 70 °C for 18 h and the resultant slurry is then filtered, washed with water, and finally dried in an oven at 60 °C. This method produces large quantities of nanocomposite and the packing density of the interlayer anion is diverse due to variable M^{2+}/M^{3+} ratios. Furthermore, a wide diversity of anions can be incorporated between the layers.

However, there is a significantly higher uptake of carbon dioxide and incorporation of unwanted hydroxide anions from the reaction mixture.

Precipitation at High Supersaturation

The precipitation at high supersaturation method requires the addition of a mixed metals salt solution to an alkaline solution that contains the interlayer anions. The materials that are synthesized by this method usually have low crystallinity, and therefore thermal treatment or aging is used after co-precipitation to increase the crystallinity of the materials.

Precipitation at Low Supersaturation

Precipitation at low supersaturation is accomplished by slow addition of mixed solutions of divalent and trivalent cation metal salts to an aqueous solution of the interlayer anion. The alkaline solution is added simultaneously to maintain the pH at selected value to lead to co-precipitation of the two metallic salts. This method gives LDHs with high crystallinity and allows control of the molar ratio, $R = M^{2+}/M^{3+}$.

IV. CHARACTERIZATION OF LAYERED HYDROXIDES

The most common analytical techniques used to characterize layered double hydroxides are Powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analyses (TGA/DTG), Scanning Electron Microscopy (SEM) and Transmission electron microscopy (TEM). Powder X-ray diffraction is used to determine purity, crystallinity, and the basal spacing of the LDHs. FTIR spectroscopy is used to identify the functional groups and chemical bands, because each functional group has its own specific wavenumbers and characteristic absorption peaks. Therefore, FTIR can be used as a supporting technique to confirm that intercalation has occurred instead of absorption. The chemical composition of the LDHs is analyzed for metal ions by inductively coupled plasma atomic emission spectrometry. The thermal stability of LDHs is measured using thermogravimetric and differential thermogravimetric analyses while the surface characterization of the LDH is carried out using surface area analysis. Scanning electron microscopy is used to determine the surface morphology of the LDHs. Optical properties and the controlled release studies are accomplished using an ultraviolet-visible spectrophotometer. Transmission electron microscopy (TEM) is used for particle size determination of layered hydroxides.

The fundamental structure of the LDH in a three dimensional view would look like Fig.1&2.

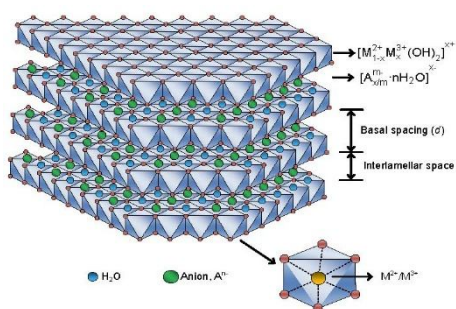


Fig.1& 2 Structure of an LDH in 3-D

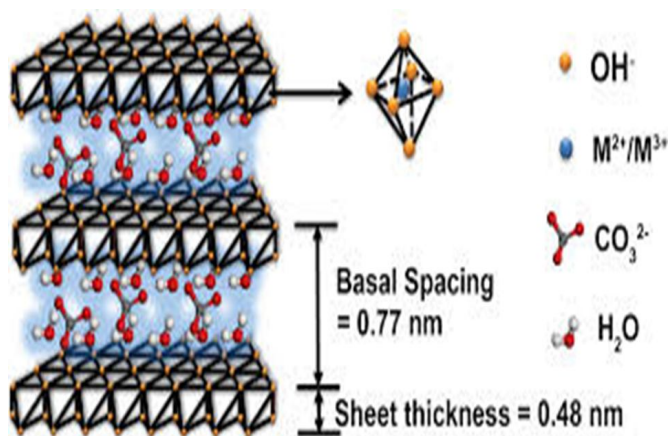


Fig. 2X-ray powder diffractogram of a ZnAl-NO3

Table 1: Interlayer spacing of the samples

Sample name	d(003) Å	d(006) Å	d(110) Å
(a) Mg-Al-NO ₃ -LDH	7.77	3.86	1.55
(b) Mg-Al-EDTA-LDH	14.98	7.38	1.56

The PXRD pattern for the LDHs show sharp, symmetric, and intense lines at low 2θ values and less intense and generally asymmetric lines at higher 2θ values. The reflections due to (003) (006) and (009) clearly shows that it is a layered material. The interlayer spacings (d) can be calculated by using the Bragg's equation $2d \sin\theta = n\lambda$ (Table1). The sharp intense lines and a doublet peak at a 2θ value of 60° indicate the existence of an ordered layered material.

IR Spectra of LDHs

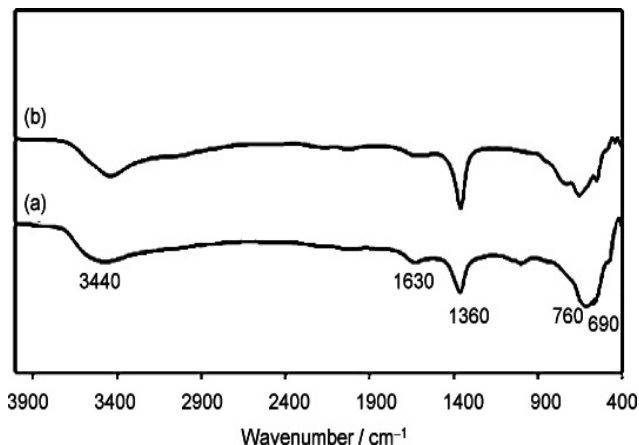


Fig. 3 FT-IR Spectra of LDHs

The infrared (IR) spectra of Mg-Al and Mg-Al:DNA are shown in Figure 3. A broad peak at 3395–3450 cm⁻¹ and a weak one at 1636–1367 cm⁻¹ correlate to ν(OH) and δ(H₂O) bands respectively. Peaks at 650–665 cm⁻¹ and 410–446 cm⁻¹ are due to M–O vibrations and M–O–H bending, where M=Mg and Al. The sharp singlet observed at 1300–1362 cm⁻¹ is due to the stretching of the carbonate ion. According to Valcheva–Traykova et al., sharp peaks at 446 cm⁻¹ and 1352 cm⁻¹, doublet peaks at 769 cm⁻¹ and 661 cm⁻¹, and a broad peak at 3396 cm⁻¹ are all characteristic of an LDH structure.

Thermogravimetric analysis

Thermal decomposition of Mg-Al-LDH involves three steps dehydration, dehydroxylation (loss of lamellar hydroxyls) and loss of interlayer carbonate. Figure 4 shows the results of thermal analysis for LDH MgAl-CO₃. The steps and sequence of thermal decomposition of LDHs can vary with the ratio of cations, but generally follow the same sequence. The first transition temperature and mass loss, below 200 °C, is associated with the evaporation of adsorbed and intercalated water molecules. The other steps, between 200 and 500 °C, refer to the decomposition of interlayer carbonate and hydroxyl groups of the lamellae (Hibino et al., 1995). Above 500 °C, the lamella of the brucite-type structure collapses and a solid solution of mixed spinel (MgAl₂O₄) and MgO, or Al₂O₃ and MgO is irreversibly formed. The first mass-loss shown in Figure 4 indicates that the synthesized material has 0.058 mol of water per unit of hydrotalcite, implying that its structural formula is $[Mg^{+2} 0.67Al^{+3} 0.33(OH)_2]^{+0.33} CO_3^{2-} \cdot 0.058H_2O$.

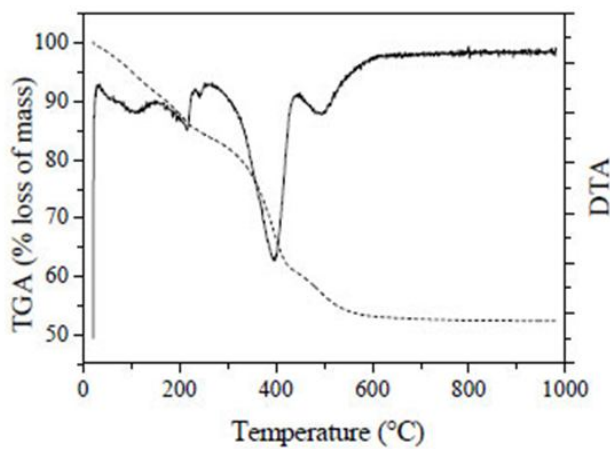


Fig. 4 Thermal analysis of the synthesized LDH

V. EXPERIMENTAL RESULTS

Result of test conducted on 27/02/2020

Sl no.	Parameters	Units	Rejected water	Treated water	Efficiency
1	pH	-	7.2	7	-
2	Conductivity	mMhos/cm	1.65	0.25	84.84
3	Total alkalinity	mg/l	1180	162	70.37
4	Total Dissolved Solids	mg/l	1080	320	85.00
5	Chlorides	mg/l	162.9	30.06	81.54
6	Hardness Calcium Magnesium	mg/l as CaCO ₃	491 389	107 189	78.20 67.91
7	Total hardness	mg/l as CaCO ₃	1080	296	72.39
8	Permanent hardness	mg/l as CaCO ₃	525	120	77.14
9	Temporary hardness	mg/l as CaCO ₃	555	176	68.28
10	Potassium	mg/l	19.2	6.2	67.70
11	Sodium	mg/l	75	12.8	82.93

Result of test conducted on 02/03/2020

Sl no.	Parameters	Units	Rejected water	Treated water	Efficiency
1	pH	-	7.1	7	-
2	Conductivity	mMhos/cm	1.60	0.27	83.12
3	Total alkalinity	mg/l	1108	68	93.86
4	Total Dissolved Solids	mg/l	1050	173	83.52
5	Chlorides	mg/l	158.2	15.4	90.26
6	Hardness Calcium Magnesium	mg/l as CaCO ₃	460 523	81 103	82.39 80.30
7	Total hardness	mg/l as CaCO ₃	1052	184	82.50
8	Permanent hardness	mg/l as CaCO ₃	515	64	87.57
9	Temporary hardness	mg/l as CaCO ₃	555	120	78.37
10	Potassium	mg/l	18.8	5	73.40
11	Sodium	mg/l	77	9.8	87.27

VI. CONCLUSION

The layered double hydroxides (LDH) were successfully synthesized by the co-precipitation method and heat treated to get Mg-Al-Oxide. Phenomenon of reducing metal ion concentration and bringing the waste water to re-usage was successfully attempted. The waste water are brought up to potable water using mixed metal oxide adsorbent material. Wastage of water during Reverse Osmosis can be successfully conserved using these adsorbent materials.

REFERENCES

[1] Ahmadpour, A., Tahmasbi, M., Bastami, T. R. & Besharati, J. A. 2009Rapid removal of cobalt ion from aqueous solutions by almond green hull. J. Hazard. Mater. 166, 925-930.

- [2] Bakr, A. A., Eshaq, G., Rabie, A. M., Mady, A. H. & ElMetwally, A. E. 2016 Copper ions removal from aqueous solutions by novel Ca–Al–Zn layered double hydroxides. *Desalin. Water Treat.* 57, 12632–12643.
- [3] Bhattacharyya, K. G. & Gupta, S. S. 2007 Adsorptive accumulation of Cd(II), Co(II), Cu(II), Pb(II), and Ni(II) from water on montmorillonite: influence of acid activation. *J. Colloid Interface Sci.* 310, 411–424.
- [4] Cantu, M., Lopez-Salinas, E., Valente, J. S. & Montiel, R. 2005 SO_x removal by calcined MgAlFe hydrotalcite-like materials: effect of the chemical composition and the cerium incorporation method. *Environ. Sci. Technol.* 39, 9715–9720.
- [5] Cardoso, L. P. & Valim, J. B. 2004 Competition between three organic anions during regeneration process of calcined LDH. *J. Phys. Chem. Solids* 65, 481–485.
- [6] Cardoso, L. P. & Valim, J. B. 2006 Study of acids herbicides removal by calcined Mg–Al–CO₃–LDH. *J. Phys. Chem. Solids* 67, 987–993.
- [7] Das, J., Patra, B. S., Baliarsingh, N. & Parida, K. M. 2006 Adsorption of phosphate by layered double hydroxides in aqueous solutions. *Appl. Clay Sci.* 32, 252–260.
- [8] Donat, R., Akdogan, A., Erdem, E. & Cetisli, H. 2005 Thermodynamics of Pb²⁺ and Ni²⁺ adsorption onto natural bentonite from aqueous solution. *J. Colloid Interface Sci.* 286, 43–52.
- [9] Elwakeel, K. Z. 2010 Environmental application of chitosan resins for the treatment of water and wastewater: a review. *J. Dispersion Sci. Technol.* 31, 273–288.
- [10] Fang, F., Kong, L., Huang, J., Wu, S., Zhang, K., Wang, X., Sun, B., Jin, Z., Wang, J., Huang, X.-J. & Liu, J. 2014 Removal of cobalt ions from aqueous solution by an amination graphene oxide nanocomposite. *J. Hazard. Mater.* 270, 1–10.
- [11] Hsu, L. C., Wang, S. L., Tzou, Y. M. & Chen, J. H. 2007 The removal and recovery of Cr(VI) by Li/Al layered double hydroxide (LDH). *J. Hazard. Mater.* 142, 242–249.
- [12] Inacio, J., Taviot-Gueho, C., Forano, C. & Besse, J. P. 2001 Adsorption of MCPA pesticide by MgAl-layered double hydroxides. *Appl. Clay Sci.* 18, 255–264.
- [13] Kandaha, M. I. & Meunier, J.-L. 2007 Removal of nickel ions from water by multi-walled carbon nanotubes. *J. Hazard. Mater.* 146, 283–288.
- [14] Karapinar, N. & Donat, R. 2009 Adsorption behavior of Cu²⁺ and Cd²⁺ onto natural bentonite. *Desalination* 249, 123–129.
- [15] Khan, T. A., Khan, E. A. & Shahjahan 2015 Removal of basic dyes from aqueous solution by adsorption onto binary ironmanganese oxide coated kaolinite: non-linear isotherm and kinetics modeling. *Appl. Clay Sci.* 107, 70–77.
- [16] Liu, Z. R. & Zhou, S. Q. 2010 Adsorption of copper and nickel on Na-bentonite. *Process Saf. Environ. Protect.* 88, 62–66.
- [17] Monser, L. & Adhoum, N. 2002 Modified activated carbon for the removal of copper zinc chromium and cyanide from wastewater. *Sep. Purif. Technol.* 26, 137–146.
- [18] Ngomsik, A.-F., Bee, A., Siaugue, J.-M., Cabuil, V. & Cote, G. 2006 Nickel adsorption by magnetic alginate microcapsules containing an extractant. *Water Res.* 40, 1848–1856.
- [19] Ngomsik, A. F., Bee, A., Siaugue, J. M., Talbot, D., Cabuil, V. & Cote, G. 2009 Co(II) removal by magnetic alginate beads containing Cyanex 272. *J. Hazard. Mater.* 166, 1043–1049.
- [20] Olgun, A. & Atar, N. 2011 Removal of copper and cobalt from aqueous solution onto waste containing boron impurity. *Chem. Eng. J.* 167, 140–147.
- [21] Orthman, J., Zhu, H. Y. & Lu, G. Q. 2003 Use of anion clay hydrotalcite to remove coloured organics from aqueous solutions. *Sep. Purif. Technol.* 31, 53–59.
- [22] Parab, H., Joshi, S., Shenoy, N., Lali, A., Sarma, U. S. & Sudersanan, M. 2006 Determination of kinetic and equilibrium parameters of the batch adsorption of Co(II), Cr(III) and Ni(II) onto coir pith. *Process Biochem.* 41, 609–615.
- [23] Roto, R., Nindiyasari, F. & Tahir, I. 2009 Removal of hexacyanoferrate (II) using Zn–Al–OAC hydrotalcite as anion exchanger. *J. Phys. Sci.* 20, 73–84.
- [24] Sanchez-Valente, J., Figueras, F., Gravelle, M., Kumbhar, P., Lopez, J. & Besse, J. P. 2000 Basic properties of the mixed oxides obtained by thermal decomposition of hydrotalcites containing different metallic compositions. *J. Catal.* 189, 370–381.
- [25] Sathyavalsal, P., Sudrajat, H., Chanthi, N. & Soknet, S. 2008 Removal of Cd(II) from aqueous solution by Ca–Al–HPO₄ layered double hydroxide. *J. Appl. Sci. Environ. Sanit.* 3, 101–108.
- [26] Turk, T., Alp, I. & Deveci, H. 2009 Adsorption of As(V) from water using Mg–Fe–based hydrotalcite (FeHT). *J. Hazard. Mater.* 171, 665–670.
- [27] Vázquez, G., Calvo, M., Freire, M. S., González-Alvarez, J. & Antorrena, G. 2009 Chestnut shell as heavy metal adsorbent: optimization study of lead, copper and zinc cations removal. *J. Hazard. Mater.* 172, 1402–1414.
- [28] Weber, T. W. & Chakkravorty, R. K. 1974 Pore and solid diffusion models for fixed-bed adsorbers. *AIChE J.* 20, 228–238.
- [29] White, B. R., Stackhouse, B. T. & Holcombe, J. A. 2009 Magnetic γ -Fe₂O₃ nanoparticles coated with poly-L-

- cysteine for chelation of As(III), Cu(II), Cd(II), Ni(II), Pb(II) and Zn(II). *J. Hazard. Mater.* 161, 848–853.
- [30] Xu, P., Zeng, G. M., Huang, D. L., Lai, C., Zhao, M. H., Wei, Z., Li, N. J., Huang, C. & Xie, G. X. 2012 Adsorption of Pb(II) by iron oxide nanoparticles immobilized *Phanerochaete chrysosporium*: equilibrium, kinetic, thermodynamic and mechanisms analysis. *Chem. Eng. J.* 203, 423–431.
- [31] Yang, W., Kim, Y., Liu, P. K. T., Sahimi, M. & Tsotsis, T. T. 2002A study by in situ techniques of the thermal evolution of the structure of a Mg–Al–CO₃ layered double hydroxide. *Chem. Eng. Sci.* 57, 2945–2953.
- [32] Yanwei, G., Zhiliang, Z., Yanling, Q. & Jianfu, Z. 2013 Enhanced adsorption of acid brown 14 dye on calcined Mg/Fe layered double hydroxide with memory effect. *Chem. Eng. J.* 219, 69–77.