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Adsorption potentials of synthesized Mg-Al double layered hydroxide (LDH) Nanoparticles

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Abstract

Mg-Al double layered hydroxides (LDH) Nanoparticles have been synthesized using a co-precipitation method and characterized using X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier Transform Infra-Red (FT-IR). The results of the XRD and SEM for the crystallite particle size of LDH-NPs (nanoparticles) were in the region of ~20 nm attributed to the smaller sized particles. The FT-IR result showed absorption bands of a possible functional group responsible for LDH formation. The adsorption analysis using Ni^{2+} in aqueous solution over 3, 5 and 10 %.w/w (corresponds to $1.7x10^{-3}$, $2.8\ x10^{-3}$ and $5.7x10^{-3}$ M respectively) Ni/LDH concentrations showed various degree of adsorption. Adsorption of ~95 % was achieved, which was measured using Microwave plasma Atomic emission spectroscope (MP-AES) instrument. The effect of pH and contact time showed Ni^{2+} optimal adsorption on the LDH-NPs at pH 10, with equilibrium established at 30 min. The absorption capacity signifies its application in catalysis, such as for dry reforming of methane, associated with high coke formations, and in environmental application for removal of heavy metals.

Keywords: Mg-Al LDH synthesis, Nano-particles, Nickel, Adsorption, Characterization

Introduction

Layered double hydroxides (LDHs) are an emergent class of inorganic lamellar nanomaterials that have attracted significant research interest due to their high surface-to-volume ratio. Their unique properties have been employed for applications in organic catalysis, sensors, drug delivery and metal adsorption [1]. LDH nano-particles are considered as low-cost and easily prepared materials, making them good candidates for research as adsorbents [2]. LDH possesses unique properties like high surface areas, porosity and anion exchange capacities (2–3 meq/g). They possess substantial thermal stability, which favour their use for metals ions adsorption [3].

Studies have described the use of adsorption material, as the most significant and economical process, due to its advantages such as simplicity, regeneration ability, and optimal operation accessibility [4].

Layered double hydroxides (LDHs) materials ($[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}A^{n-}_{x/n}\cdot mH_2O$) are very attractive systems due to their robust structure. It can be finely modulated by suitable selection of metal cations, functional interlayer compensating anions, ratio of M2 /(M2 + M3), as well as the relatively weak interlayer bonding [5]. They are built of positively charged brucite-like layers linked by exchangeable anions (a promising property for adsorption). Nitrate anions, contained in the interlayer space, are used for sorption of cationic ions from aqueous media such as the Ni^{2+} [6].

There are numerous metals, which are potentially toxic to humans and to ecology [7, 8] but which can be used in industries for catalysis [9, 10]. These includes nickel (Ni), manganese (Mn) chromium (Cr), palladium (Pd), zinc (Zn), etc. [11] and their nano-particles [12]. As such, LDH can be used either as an adsorbate or as a support for catalytic operation in industrial processes.

The aim of this work is to synthesize and to characterize LDH nano-particles. The study investigated the adsorption ability of LDH as adsorbent for Ni^{2+} from aqueous solution. Furthermore, the effects of operational parameters such as time and pH on the adsorption process are investigated, very important parameters to determine effectiveness of the LDH as an adsorbent and/or as catalyst.

Experimental

Materials

All chemicals used in this study were of analytical grade. Magnesium nitrate [$Mg(NO_3)_2.6H_2O$], aluminum nitrate [$Al(NO_3)_2.9H_2O$], sodium hydroxide (NaOH) and other solvents used were obtained from general laboratory store Department of Pure and Industrial Chemistry, Bayero University Kano, and were supplied by Sigma Aldrich. Nickel nitrate [$Ni(NO_3)_2.6H_2O$] was purchase from Strem Chemicals, and Formamide from Merck.

Instrumentation

X-Ray diffractometer (XRD), scanning microscope (SEM), Fourier Transform Infra-Red (FT-IR) and microwave plasma atomic emission spectrometers (MP-AES) have been used for analytical studies.

$Mg^{2+}/Al^{3+}/NO_3^-$ —LDH Nano-particle preparation

The Mg-Al LDH nanosheet material was prepared by co-precipitation as described by

[12], with little modification. The Mg was the carrier and the Al was the tracer. Two solutions were prepared: the first solution contained $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ dissolve in dist. H_2O and made up 1cm^3 with a molar ratio 4:1 Mg/Al , this was transferred into a syringe. The second solution contained, $NaNO_3$ dissolved a 23% aqueous solution of formamide (vol/vol) based on a modified synthesis protocol reported by Bayu and coworkers [14]. 10cm^3 of the 1M NaOH was then added to adjust the pH to ~12 and the solution was made up to 49cm^3 using distilled water while stirring on a magnetic stirrer. The 1cm^3 Mg/Al metal precursor solution (in the syringe) was added quickly (~10 s) into the second solution under vigorous stirring (1400 rpm at ambient conditions) for ~ 1min followed by centrifugation at 3000 rpm. The gel-like LDH precipitate was washed 3 times with distilled H_2O to remove excess Na^+ ions.

LDH Adsorption Study

The adsorption studies were carried out using the prepared LDH. The Ni^{2+} concentrations were varied as percentage loading with respect to the adsorbent LDH (3, 5 and 10 %.w/w) this is taking into consideration the assumption that all of the Ni^{2+} is adsorbed. The Ni^{2+} were adsorbed under static conditions with continuous stirring, the volume of the aqueous phase was maintained at 100 cm^3. For each Ni adsorption analysis, three solutions were made at 3 different pH parameters (i.e. pH 7, 10, and 13). The solutions were stirred at different time intervals (0-120 mins). After the adsorption, the stirred solutions were centrifuged (at 4000 rpm) and the supernatant analyzed for the concentration of Ni using MP-AES. The value of the metal adsorption (a_s μmol/g) and the % adsorption (A %) were calculated according to eqn 1and 2 respectively.

$$a_s = (C_o - C_{eq})\frac{V}{m} \ldots\ldots\ldots\ldots\ldots 1.1$$

$$A = \frac{(C_o - C_{eq})}{C_o}\, x\, 100 \ldots\ldots\ldots\ldots 1.2$$

C_o = initial concentration

C_{eq} = eqilibrium concentration

V = aqeuos phase volume

m = weight of Ni

Analytical methods

The synthesized LDH-Nps were characterized using XRD, SEM and FT-IR. The X-ray diffraction pattern of LDH-NPs was recorded using X-ray diffractometer (Rigaku D/Max-IIIC) using CuKa (1.662 Å) radiation set at 40 kV and 20 mA. The morphology and particle size of LDH nanoparticles were investigated using scanning electron microscopy (SEM JOEL JSM-7600F) with a magnification range 8000-9000, resolution 120 Å and acceleration of 15kV, and transmission electron microscope (JEM-ARM200F-G TEM). The LDH were grafted onto a silica support at different LDH concentrations (10, 50 and 100 %) for better analysis. The FTIR analyses were determined with an FT-IR spectrometer (FTIR-Cary 630 from Agilent technologies and the spectra were recorded in the wavelength interval range of 4000-600 cm^{-1} on resolution of 4 cm^{-1}.

Results and Discussion

The LDH Adsorption studies

The results obtained from the adsorption studies are presented in table 1. They show that the LDH nano-particles are a good adsorbent for Ni^{2+}, with an adsorption of 266 μmol/g, which is equivalent to ~95 % adsorption and was obtained at pH 10 using 5 % Ni loading.

Table 1: Ni adsorption using 3, 5 and 10 % loading on LDH at various pH for 30 min

pH	*Adsorption of Ni^{2+} by LDH (μmol/g)*		
	3% ($1.7x10^{-3}$ M)	5% ($2.8 x10^{-3}$ M)	10 % ($5.7x10^{-3}$ M)
7	102	196	428
10	153	266	559
13	136	238	502

The profile for the percentage adsorption is presented in figure 1. The result shows that, better adsorptions of the Ni^{2+} on the LDH are obtained at pH 10. This could be attributed to the fact that pzc of a solid surface is necessary for specific adsorption purpose (i.e. positively charged below pzc and negatively charged above pzc). Therefore, since LDH has a pzc of 12, it is expected that substantial amount of Ni^{2+} will be adsorbed at pH=10. Meanwhile, it is also noticeable that the higher the concentration of the Ni^{2+} present in the adsorption aqueous phase, the more LDH-NPs that are adsorbed. Higher adsorption (559 μmol/g) is observed with the 10 % Ni concentration than at lower concentrations.

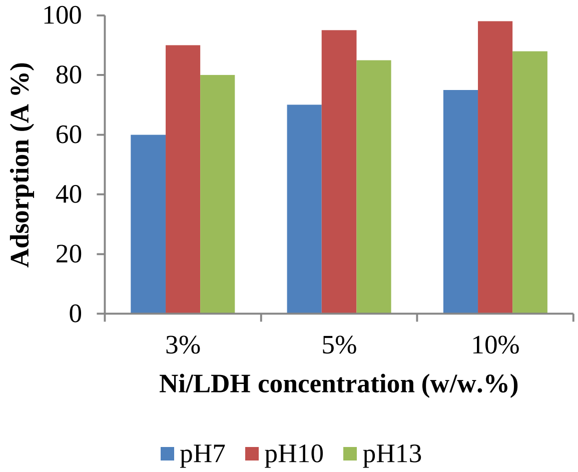

Figure1: comparative percentage adsorption of Ni^{2+} at different pH and concentration

Effect of pH on the Ni adsorption on the LDH

The pH is an important parameter in adsorption studies. Figure 2 shows that maximum values of Ni adsorption are achieved at pH 10. This testifies the high performance adsorption of the LDH-NPs in anionic forms (i.e. pH 10 = negatively charged LDH, according to pzc). Generally, the results show the significant effect of pH on the adsorption process of the LDH, showing variable degree of adsorption with respect to the Ni concentration. This is similar to the findings of Gonzalez and coworkers [15]

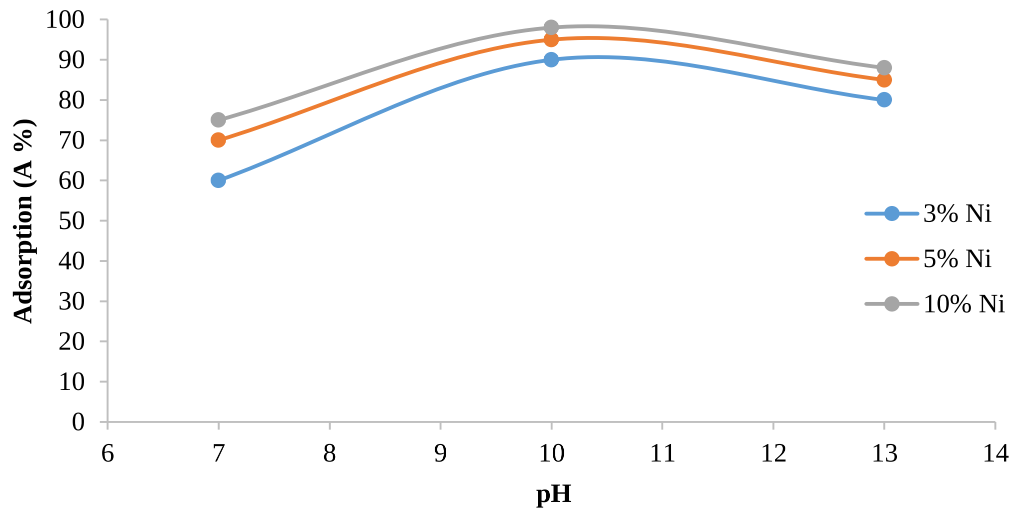

Figure 2: Influence of pH on Ni adsorption with different concentrations

Effect of contact time on Ni^{2+} adsorption on the *LDH*

Contact time or wet time is the period the adsorbate solution is left in contact with the adsorbent. It is a very important parameter in the adsorption process. The data obtained for the contact time of Ni adsorption on the LDH is presented in figure 3. It was clearly observed that equilibrium was established at ~30 min, for all the studied pH levels. About 98 % adsorption was attained at pH 10 with 10 % loading. This shows that an excellent amount of the Ni^{2+} can be adsorbed on the LDH-NPs in a very short time and is an important parameter in the field of catalysis [16].

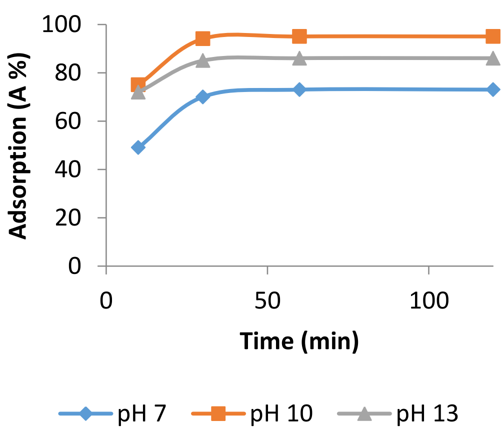

Figure 3: Effect of time on Ni adsorption using 10%.wt loading

Characterization of the LDH-Ns Material

X-ray diffraction Analysis (XRD)

The XRD pattern obtained from LDH-NP (fig. 5) exhibits the characteristic reflection of layered double hydroxides the diffraction peaks were indexed to hexagonal lattice rhombohedral 3R Symmetry [18].

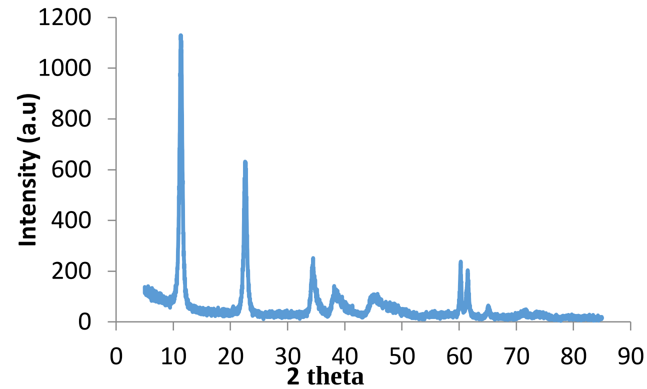

Figure 5: X-ray diffraction profile of the Mg-Al LDH adsorbents

The XRD diffraction indicates that nanocrystals are present in the sample. The diffraction peaks are located at 11.3^0, 22.5^0, 34.5^0, 38.5^0, 43.9^0, 60.2^0, $61.3^0$and 64.4^0. The average crystallite size of the LDH-NPs is calculated using Debye Scherrer's formula:

$$\underline{D} = 0.89\lambda / \beta\cos\theta$$

Where 0.89 as Scherrer's constant value, λ is the wavelength of X-rays, θ is the Bragg diffraction angle, and β is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plane (201). On substituting the values of $\lambda = 1.6624^0$, $\beta = 0.121$, $\cos\theta = 0.6161$ in Debye Scherrer's formula $\underline{D} = 19.84$ nm. The average particle size of the sample was found to be ~26.34 nm which is derived from the FWHM of more intense peak corresponding located at 11.3^0 using the above formula. The value is close to those reported in the

Scanning electron microscopy (SEM)

Fig. 4 represents the SEM images of LDH nanoparticles at different concentrations supported on silica (i.e. 10%, 50%, and 100% as prepared LDH mounted on the silica support). The SEM images show differences according to the LDH loading on the silica support. The silica without LDH showed a clear silica surface, while others showed various coverages based on the LDH % loading. The LDH showed a randomly oriented nano particle and was widely spread on the silica (20-50 nm in size). The building block layers of the LDH exhibited a typical oval like morphology, but due to the large specific surface area and high surface energy, some nanoparticles are aggregated [12, 17,].

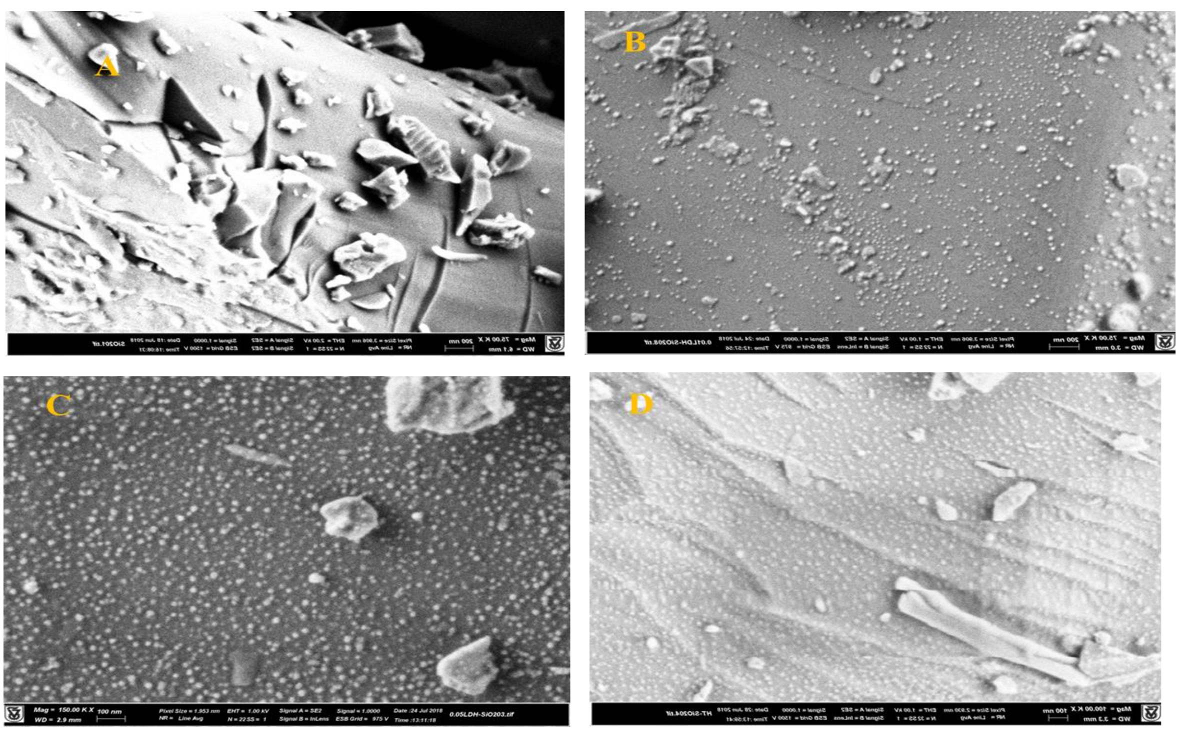

Figure: 4 SEM Micrograph of (A) fresh silica support, (B) 10 % LDH on silica (C) 50 % LDH on silica (D) 100 % w/w LDH on silica

Fourier Transform Infra Ray Spectroscopy (FT-IR) Analysis

To examine the LDH-NP structure, both on the metal oxide support and LDH as synthesized, FT-IR analytical analysis was performed on the LDH, the result provided us with the detailed information about the main functional groups responsible for the formation of Mg-Al LDH and other important functional groups, as presented on the figure 6. The spectra shows adsorption bands due to hydroxyl groups (-OH), water molecule (H_2O), and Mg—O, Al—O, and Mg—O—Al, stretching vibrations which are typical of LDH material and have been already reported in the literature [20].

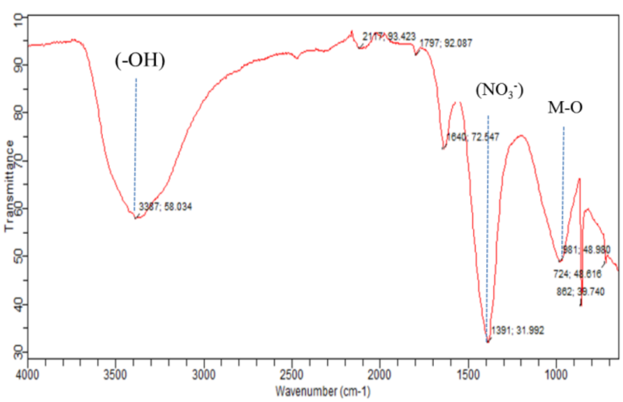

Figure 6: FTIR absorption bands of the Mg-Al LDH,

The intense and broad peak at approximately 3449 cm^{-1} could be attributed to the stretching vibration of the O–H group from both the hydroxide layers and interlayer water [21]. The corresponding band close to 1665 cm^{-1} could be attributed to bending vibration of the H–OH molecules. A strong absorption band near 1377 cm^{-1} corresponded to nitrate anions [22].

Summary and Conclusion

The Layered double hydroxides (LDHs) are an emergent class of inorganic lamellar nanomaterials with a high surface-to-volume ratio, this enables them to adsorb specific materials. They are considered generally as promising materials due to their high chemical versatility, associated with a tunable anionic exchange capacity [23]. The unique physical and chemical properties render the LDH as an exceptional candidate for the adsorption of numerous metals with versatile physical and chemical properties. The unique properties of LDH render adsorption of metals coordinately adsorbed at their edge, which contains its most active sites. Furthermore, Adsorption on the edge of the crystalline is much more favorable compared to the crystal surface. Therefore, the edge of the crystalline is a more active site [24]. This shows that the LDH could be a quick adsorbent and can adsorb metal even at high concentrations. It is revealed in this work that the LDH adsorption capacity depends on the concentration of Ni metal where 153, 266 and 559 μmol/g were adsorbed using 3, 5 and 10 wt.% loading respectively at the same adsorption conditions

The removal efficiency of the studied Ni^{2+} from aqueous media using Mg-Al LDH-NPs Material was successful. The results of the study reveal that LDH have adsorption activity over Ni^{2+} ions. This property elucidates the rational for the effective use of the LDH material as adsorbents, with potential usage in catalysis. The adsorption activity of the LDH-Ns material was strongly dependent on pH, concentration and contact time. These parameters significantly affect the adsorption capacity of the LDH. Our finding shows that working in a high pH (~10) is optimal for Ni adsorption on the LDH; in particular (> 95% adsorption) was achieved. Based on the conducted synthesis method, the SEM analysis confirmed making LDH nano particle of ~ 20 nm and nicely grafted on silica support. This is also particularly interesting in designing a special catalyst.

Conflict of Interest

The authors declare no competing interests

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