Studies on the Isotherm, Kinetics and Thermodynamic Aspects of Dye Adsorption from Aqueous Solution by Using Layered Double Hydroxide Based Sorbents

A Thesis

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Chapter-VII

General Conclusion

The present study successfully synthesized surfactant-modified LDH, Zr-modified LDH, biomass ash-LDH composites, and ternary CaNiAl-LDH, which are further employed in dye sorption experiments. All the adsorbents were prepared via simple co-precipitation methods, except in the synthesis of biomass ash modified LDH, where the burning of coconut husk to ash followed by co-precipitation with LDH was carried out. The as-synthesized adsorbents are characterized by using powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FT-IR), Scanning emission microscopy (SEM), Energy dispersive X-ray (EDX), Tansmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Brunauer-Emmett-Teller (BET) techniques. The modified LDH synthesized in this study was specifically applied for removing five dyes, representing two classes: cationic dyes (Methylene blue, malachite green) and anionic dyes (Congo red, methyl red, methyl orange). The following conclusions are drawn from the detailed adsorption studies:

The successful formation of layered structures in all the adsorbents, viz., ZrO_2/MgAl-LDH, CuAl/SDS-LDH, CHA/CoAl-LDH, CHA/NiAl-LDH, and CaNiAl-LDH was confirmed by the diffracted peaks observed in the PXRD spectrum corresponding to indexed planes at 003, 006, 009, 015, 018, 110, and 113. However, modification with surfactants in the LDH structure leads to shifting of the peaks at lower angle, which results in increasing the interlayer distance of CuAl/SDS-LDH, and the theoretically calculated length of basal spacing was found to be 14 Å. The observed results suggest intercalation of sodium dodecyl sulfate molecule in the inter lamellar region as well as assemblage on the external surface of LDH. Accounting to LDH thickness (0.48 nm) and the length of SDS chain, which is taken as 1.78 nm, the possible alignment of SDS inside the layer sheets is tilted with respect to LDH sheets. Moreover, the peak observed in CHA at 2θ values (26.51, 38.29, 39.14, 41.29 and 58.58) was also manifested in the CHA/CoAl-LDH composite, which further implies the association of carbonaceous material derived from coconut husk with the LDH structure.

The morphological analysis using SEM techniques also further corroborates the formation of porous and sharp sheet-like LDH structures in ZrO_2/MgAl-LDH, CuAl/SDS-LDH, and hexagonal shapes (CHA/CoAl-LDH), and circular flower-like particles (CaNiAl-LDH) were also evident. The TEM analysis of the CHA/CoAl-LDH composite also revealed an irregular shape, and the typical crystalline hexagonal CoAl-LDH particles were well assembled on the carbon matrix.

The N_2 adsorption-desorption curves manifested a type-IV isotherm with an H-3 hysteresis loop in all adsorbents, except H-4 hysteresis in ZrO_2/MgAl-LDH. The specific surface area of biomass ash was relatively lower than that of pristine LDH; however, an intermediate surface area was found in all samples, and the determined BET surface area lies in the range of 4.17-74.05 m^2/g. The constituent's elements detected by the EDX technique in the synthesized adsorbents are listed in **Table.VII.1.**

The various experimental parameters, including isotherm, kinetics, and thermodynamic parameters, obtained in this study are summarized in **Table.VII.2**. The adsorbents such as ZrO_2/MgAl-LDH, CuAl/SDS-LDH, CHA, CHA/CoAl-LDH, CHA/NiAl-LDH, and CaNiAl-LDH showed the q_{max} values of 169.42, 411.47, 943.39, 666.4, 11.82, and 135.21 mg/g, corresponding to the adsorption of CR, MR, MG, MB, and CR dyes, respectively. The adsorbents CHA (943.39 mg/g) and CHA/CoAl-LDH (666.4) showed the highest monolayer adsorption capacity compared to other adsorbents. However, the isotherm studies suggest that the adsorption process takes place via monolayer formation in almost all adsorbents and can be best described according to the Langmuir model. The kinetic studies of all adsorbents have been validated and well described based on a pseudo-second order model. The evaluated q_{e2} values obtained from the pseudo-second order model for adsorbents ZrO_2/MgAl-LDH, CuAl/SDS-LDH, CHA, CHA/CoAl-LDH, CHA/NiAl-LDH, and CaNiAl-LDH are 130.89, 69.48, 276.24, 242.71, 14.32, and 41.15 mg/g, respectively.

In this study, the predominant adsorption mechanism responsible may be accounted for due to the presence of electrostatic attraction and H-bonding, but in CHA/CoAl-LDH and CHA/NiAl- LDH, additional interactions such as n-π, π-π, ion exchange, pore diffusion etc., may

exist. However, the sorption ability of LDH is due to its hierarchical positively charged surface having a strong affinity for anionic dyes, while in biomass ash, the existence of a negatively charged surface generally favours cationic dyes.

The thermodynamic studies of CR dye sorption over ZrO_2/MgAl-LDH revealed that with increasing temperature from 303 K to 333 K, the negative value of ΔG (-3.06 to -6.54 KJ/mol) was observed, indicating the spontaneous nature of sorption, and the positive ΔH=31.51 KJ/mol values represent an endothermic process. Similarly, sorption of dyes such as MR, MG, MB, CR, and MO over CuAl/SDS-LDH, CHA/CoAl-LDH, CHA/NiAl-LDH, and CaNiAl-LDH adsorbents also followed spontaneous and endothermic process.

The uptake of dyes over the adsorbents was influenced by the solution pH. The maximum removal percentage and optimum pH of the solution for the adsorbate-adsorbent system, viz., CuAl-LDH-MR (86%, pH-4), CuAl/SDS-LDH-MR (96.93%, pH-4), ZrO_2/MgAl-LDH-CR (81.96%, pH-4), CHA-MG (98.39%, pH-10), CHA/CoAl-LDH-MG (98.16%, pH-10), CaNiAl-LDH-CR (97-95.7%, pH-4-7) and CaNiAl-LDH-MO (98.9%, pH-4-5) were noticed. Therefore, the cationic dyes are favourably adsorbed in the basic medium, while the anionic dyes prefer the acidic nature of the medium.

The reusability studies of the adsorbents were conducted, and the percentage removal for the adsorbents ZrO_2/MgAl-LDH, CuAl/SDS-LDH, CHA, CHA/CoAl-LDH, and CaNiAl-LDH lies within the range of 97.19-59.04 % (1^{st} -5^{th} cycle), 98-28.86 % (1^{st} -4^{th} cycle), 95-71% (1^{st} -3^{rd} cycle), 94.2-60.3 (1^{st} -3^{rd} cycle), and 95.73-75.99% (1^{st} -5^{th} cycle), respectively. The best reusability of ZrO_2/MgAl-LDH and CaNiAl-LDH may be attributed due to less leaching of adsorptive sites.

Table VII.1: The elemental composition (atomic weight %) of all the synthesized adsorbents.

Adsorbents	Elemental Composition (Atomic weight %)														
	Zr%	Ni%	Cu%	C%	O%	Co%	S%	Al%	Na%	Mg%	K%	Ca%	Si%	Cl%	P%
ZrO_2/MgAl-LDH	13.92	-	-	-	55.20	-	-	11.50	-	19.38	-	-	-	-	-
CuAl-LDH	-	-	18.23	-	71	-		-	-	-	-	-	-	-	-
CuAl/SDS-LDH	-	-	6.87	42.77	-	-	4.24	42.76	-	3.35	-	-	-	-	-
CHA	-	-	-	38.55	39.62	-	-	-	2.48	2.66	5.81	0.90	5.61	0.35	0.32
CHA/CoAl-LDH	-	-	-	32.63	47.18	9.24	-	3.08	1.48	1.07	0.18	0.50	0.97	0.11	0.17
CHA/NiAl-LDH	-	9.63	-	24	40	-	-	1.99	6.64	1.36	5.74	2.71	1.94	2.12	0.51
CaNiAl-LDH	-	48.72	-	0.27	36.63	-	-	7.75	-	-	-	2.02	-	-	-

LDH = Layered Double Hydroxide, SDS = Sodium Dodecyl Sulfate, CHA = Coconut Husk Ash

Table VII.2: The isotherm, kinetics, thermodynamics, adsorption mechanism and synthetic method of all the studied adsorbate-adsorbent system are listed.

Adsorbent	Synthetic method	Dyes	Isotherm	Kinetics	q_{max} (mg/g)	Thermodynamics
ZrO_2/MgAl-LDH	Co-precipitation	Congo red	Langmuir, Redlich-peterson	Pseudo-second-order	169.42	Endo
CuAl-LDH	Co-precipitation	Methyl red	Langmuir	Pseudo-second-order	209	Endo
CuAl/SDS-LDH	Co-precipitation	Methyl red	Langmuir	Pseudo-second-order	411	Endo
CHA	Combustion of coconut husk	Malachite green	Langmuir	Pseudo-second-order	943.39	Endo
CHA/CoAl-LDH	Combustion/ co-precipitation	Malachite green	Langmuir	Pseudo-second-order	666.40	Endo
CaNiAl-LDH	Urea hydrolysis	Congo red	Langmuir	Pseudo-second-order	135.21	Endo
CaNiAl-LDH	Urea hydrolysis	Methyl orange	Langmuir	Pseudo-second-order	40.93	-
CHA	Combustion of coconut husk	Methylene blue	Langmuir	Pseudo-second-order	32.13	Endo
CHA/NiAl-LDH	Combustion/ co-precipitation	Methylene blue	Langmuir	Pseudo-second-order	11.82	Endo

VII.1 Future scope:

1. Further investigations will be required to determine the mechanisms and sites of adsorption of dyes on LDH-based adsorbents.
2. It is also noted that both CHA and CHA/NiAl-LDH have low adsorption abilities for the cationic dye methylene blue. Thus, it is required to test several modified LDH materials to determine the parameters that will boost dye adsorption capability.
3. A significant number of Zr-based adsorbents were reported only for metal adsorption, but the synthesis of Zr-modified LDH could be useful in removing both metal and organic dyes. Thus, further investigation of Zr-modified adsorbent is required for more efficient and wide application in both organic and inorganic pollutant remediation.
4. The adsorbents such as CHA and CHA/LDH composite can be further employed as catalyst in studying organic reactions.
5. To comprehend the application of LDH-based adsorbents in industry, adsorption experiments need to be carried out in multi-component systems comprising different kinds of dyes, and the results need to be contrasted to those found in single-component systems.

List of publications/seminar presentation

1. Brahma, D.; Saikia, H.; (2022) Synthesis of ZrO_2/MgAl-LDH composites and evaluation of its isotherm, kinetics and thermodynamic properties in the adsorption of congo red dye. ***Chemical Thermodynamics and Thermal Analysis,*** 7: 100067, **(Elsevier)**

2. Brahma, D.; Nath, H.; Borah, D.; Debnath, M.; Saikia, H.; (2022) Coconut Husk Fabricated CoAl-Layered Double Hydroxide Composite for the Enhanced Sorption of Malachite Green Dye: Isotherm, Kinetics and Thermodynamic Studies, ***Inorganic Chemistry Communications***,144: 109878. **(Elsevier)**

3. Brahma, D.; Saikia, H.; (2023) Surfactants assisted synthesis of CuAl-sodium dodecyl sulfate layered double hydroxide and its adsorptive removal methyl red dye from aqueous solution, ***Inorganic and Nano-Metal Chemistry***, **(Taylor & Francis)**

4. Brahma, D.; Nath, K.P.; Borah, Patgiri, M.; Saikia, H.; (2022) Synthesis of ternary CaNiAl-Layered Double Hydroxide as a potential adsorbent and its effective removal of Congo red dye, ***Asian Journal of Chemistry***, 34: 3215-3223. **(Asian Publication Corporation)**

National and International Conferences

1. Surfactants assisted synthesis of CuAl-sodium dodecyl sulfate layered double hydroxide and its adsorptive removal of methyl red dye from aqueous solution**.** National Conferences on Advances in Sustainable Chemistry and Material Science (ASCMS-2022), Bodoland University, 29-30th April, 2022.
2. Synthesis of ternary CaNiAl-Layered Double Hydroxide as a potential adsorbent and its effective removal of Congo red dye from aqueous solution. International Conference on Emerging Trends in Nanomaterials Science and Technology, Department of Science and Humanities, NIT Nagaland, 27-29th January,2022.
3. Synthesis of LDH derived CuAlO mixed metal oxide. International e-poster Conference on Current Outlook in Material Science and Engineering (COMSE-2K20), Department of Chemistry, Bodoland University, 15-16th May, 2020.
4. Synthesis of ZrO_2/MgAl-LDH composites and evaluation of its isotherm, kinetics and thermodynamic properties in the adsorption of congo red dye. National Conference on Science and Technology for Sustainable Development (STSD-2022), Science College, 9-10th September 2022.
5. Coconut Husk Ash Modified CoAl-Layered Double Hydroxide Composite and its application in Dye Remediation from Aqueous Solution. International Conferences on Current Trends in Chemical Sciences for Sustainable Living, Shyam Lal College, 4th April, 2024.