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Removal of Isolan Dark Blue 2SGL-01 on Calcined $(\text{CO}_3)_{0.22}/\text{Cl}_{0.55}\text{-Mg}_{3.67}\text{Zn}_{0.26}\text{Al}$ Layered Double Hydroxide

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ABSTRACT

The removal of the residual dyes from waste effluents of dyeing is mandatory to achieve safe disposal to water body particularly in case of heavy metal complex dyes such as the industrial colorant Isolan Dark Blue 2SGL-01 (IDB). The adsorption of IDB was studied on the newly reported calcined $(\text{CO}_3)_{0.22}/\text{Cl}_{0.55}\text{-Mg}_{3.67}\text{Zn}_{0.26}\text{Al}$ layered double hydroxide (CLDH10) from aqueous solutions. The adsorption parameters; initial pH, equilibration time, dosage of adsorbent and concentration of IDB, were studied. Optimum pH for adsorption was at pH=8.7 and time of shaking 6 h. A pseudo-second order rate kinetics was observed for the adsorption process which follows the Langmuir-type adsorption isotherm with a monolayer capacity of 423.7 mg g^{-1} . CLDH10 was confirmed to efficiently remove > 99% of IDB. The loaded IDB was recovered in a single-batch process from CLDH10 with an elution efficiency of 29.4% using $1 \text{ mol L}^{-1} \text{ Na}_2\text{CO}_3$ at 50°C .

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INTRODUCTION

Dyes, pigments and paints production has significantly increased worldwide in recent years. The production of colorful new materials that are "environmentally friendly," is still a hope as many of the dyes (organic, inorganic or complex) are toxic that cause water pollution if discharged into the environment without treatment, which poses a serious threat to the environment [1,2]. Some of the remaining dyes are non-biodegradable because of complex molecular structures, and in particular the case of heavy metal complex dyes, making it more stable and non-degradable [3,4]. Many of these complex compounds are also toxic and can cause direct damage or affect the different living environment capabilities [5,6].

Treatment techniques of dyeing liquid waste are applied such as, photocatalytic [7,8], sonochemical [9] and electrochemical [10] degradation, ultrafiltration [11], membrane separation [12] and biological treatment [13, 14] although, they have several disadvantages. For example, discoloration process may not be enough to remove the threat of deteriorating components as is the case with heavy metals - acid dye Isolan Dark Blue 2SGL-01 (IDB, Fig. 1) [14]. Moreover, the products may be toxic in itself, rather than the high cost and the difficulty of applying.

Adsorption is one of the possible ways to remove the dyes under the "soft" conditions, without the generation of secondary hazardous materials. It is an effective economic process to remove dyes, pigments and other materials and dyes. Also, they are characterized by low initial cost, simplicity, and ease of operation, the possibility of restoring the dye and indifference toward toxic substances [15, 16].

Recently, it has been many methods to develop cheaper and effective adsorbent study. Many unconventional low-cost adsorbents, including natural materials, have been proposed. Generally, suitable adsorbent should achieve the effective removal of a wide range of dyes, high capacity and rate of absorption, high selectivity for different concentrations and environment-friendly water parameters characteristics [5, 17].

Layered double-hydroxides (LDHs), known also as hydrotalcite compounds such as, HTs, are able to host anionic dyes such as methyl orange [18, 19]. Bouraada *et al.* [20] reported the removal of Green Bezanyl-F2B dye from aqueous solutions using Mg-Al LDH as adsorbent. LDH containing carbonate, $3(\text{Mg,Zn})\text{-Al}$ as adsorbent to remove Astrazon Remazol Brilliant Blue and Red direct from aqueous solutions [6]. The removal

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of acid orange 10 was also possible on various calcined MgAl-LDH with the capabilities of the separation of up to 0.9 mmol g⁻¹ [21].

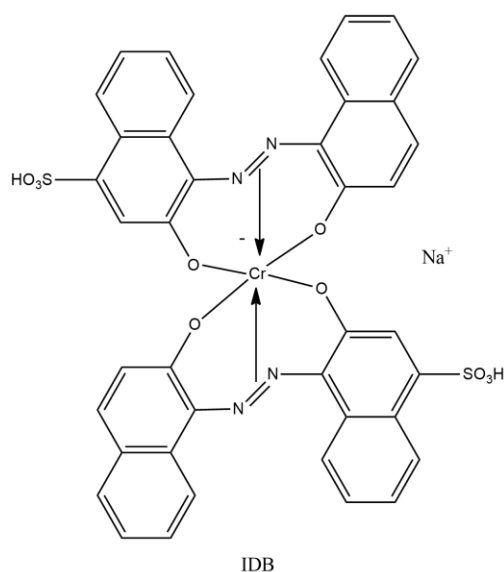


Fig. 1: Structure of IDB.

Al LDH have a high affinity for hosting sulfonate to the extent that, unlike most of the anions, are not displaced by carbonate which indicates that there is coordination between the oxygen bonds sulfonate and aluminum ions [22]. In addition, recently, the synthesis of LDH-(CO₃)_{0.22}/Cl_{0.55}-Mg_{3.67}Zn_{0.26}Al (LDH10) was reported with an adsorption efficiency of 46.2 mg g⁻¹ of IDB (7.6% of the theoretical capacity 212 mEq per 100 grams) [23] that has been increased on calcination to 314 mg g⁻¹ (24.1% of the theoretical capacity 0.455 mEq per 100 grams). This study was conducted to investigate the adsorption of IDB to CLDH10.

2. Experimental:

2.1. Materials:

The materials used in the synthesis of LDH's were of analytical grade pure from ALPHA CHEMIKA, Mumbai – India, and used as received. IDB (generic name 'Acid Blue 193', molecular formula C₄₀H₂₂CrN₄O₁₀S₂H₂Na and molecular weight 859.76) and the nylon conditioner Iyogen@NH (as leveling agent) were kindly supplied by Mr. Hamdy Abdel Sadek, DyStar, Egypt and Prof. Dr. Abdalla A. Mousa, Dying, Printing and Textile Auxiliaries Department, National Research Centre, Dokki, Giza, Egypt, respectively. The IDB stock solutions were prepared by dissolving accurately weighed IDB in distilled water to a concentration of 2000 µg mL⁻¹. The experimental solution was obtained by appropriate dilutions to different initial concentrations.

2.2. Equipments:

Powder XRD spectra were recorded on a Bruker AXS D8 ADVANCE from 2θ 4 to 80° using Cu_{Kα} source (λ = 1.54Å). Electronic spectra were recorded on a Unicam UV/Vis 2100 and NUICO 1200, USA, UV-Vis spectrophotometers using a 1 cm quartz cell. The final concentration of the dye IDB in solution was measured by UV-vis spectrometry at wavelength of 586 nm [14, 23]. Standard IDB dye solutions of known concentration were prepared in the range 1-70 mg L⁻¹, which give linear calibration curve. A blank sample containing no dye and another containing dye solution were measured together with every batch of sample run. FTIR spectra were recorded on a Nicolet iS10, Thermo-Fisher Scientific, USA, using KBr pellet. The pH of each sample solution was adjusted by NaOH and HCl solutions, by using a Hanna Instruments, 8519, Italy, pH/mV meter with an expanded scale and having an accuracy of ±0.1.

2.3. Methodology:

2.3.1. Synthesis of LDH's:

The co-precipitation procedure described previously [23] was followed. An aqueous solution of Mg(II), Zn(II), and Al(III) chlorides with initial metal ratios of 2.7:0.3:1 were prepared by coprecipitation at pH = 10, by simultaneous dropwise addition of 100 mL of a total of 2.5 mol L⁻¹ of the mixture of the metal chlorides to a basic carbonate solution. The resulting precipitate was washed repeatedly for 10 times with distilled water, then dried at 70°C for 48 h, kept in desiccator and coded LDH10. Calcined LDH10 (CLDH10) was obtained by thermal treatment of LDH10 at 450°C for 3 h in air, cooled to room temperature and kept in desiccator.

2.3.2. Adsorption study:

CLDH10 was tested as adsorbent for IDB using batch-mode experiments, which were carried out in 100 ml glass flask at $30 \pm 2^\circ\text{C}$, otherwise stated. Typically, 25 mg of CLDH10 was shaken for 6 h in 25 ml of aqueous IDB solution with an initial concentration 400 mg L^{-1} and the applied initial pH was in the range 4 - 10. Then, the suspensions were left for 24 h to ensure equilibration, centrifuged and the residual IDB concentration in the clear solution was measured by UV.

To study the effect of time of shaking, 25 mg of each adsorbent was suspended in 25 mL of initial concentration 100 mg L^{-1} of CLDH10, at the favorable initial pH 8.7 which resulted from the pH study and the final concentration was measured at different time intervals.

The effect of initial concentration was studied by suspending 25 mg of the sorbent with 25 mL of IDB with initial concentrations 100 - 1000 mg L^{-1} of CLDH10 mg L^{-1} at pH 8.7. Then the suspensions were shaken for 6 h, filtered after 24 h and the residual IDB concentration was measured by UV.

Effect of adsorbent dose on the adsorption of 25 mL of IDB was performed applying doses 12.5 - 150 mg of sorbent with an initial concentration 500 mg L^{-1} of CLDH10. The suspensions were then shaken for 6 h and the final IDB solution was centrifuged after 24 h.

The amounts of adsorbed IDB (mg g^{-1}) at equilibrium (q_t) were calculated from the mass balance expression given by the equation:

$$q_t = \frac{(C_0 - C_t)}{m} V \text{ (mg/g)} \quad (1)$$

Where C_0 and C_t , are the liquid-phase concentrations (mg L^{-1}) of IDB at initial and equilibrium time, respectively. V is the volume of solution (L) and m is the mass of adsorbent (g). In order to assess the reproducibility and error of the experimental results, all measurements were performed in triplicate runs. It was found that the relative standard deviations are about $\pm 3\%$.

Adsorption capacity (q_e) was calculated using Eq. (2):

$$q_e = \frac{(C_0 - C_f)}{m} V \text{ (mg/g)} \quad (2)$$

where; C_f (mg L^{-1}) are the final concentrations of dye solution after aging for 24 h. The removal efficiency, R (%), was calculated using Eq. (3):

$$R = \frac{(C_0 - C_f)}{C_0} 100 \text{ (%) } \quad (3)$$

For release study, 25 mg of CLDH10 was suspended in 25 mL of initial concentration 100 mg L^{-1} of IDB at pH 8.7, and shaken for 6 h, left for 24 h and the final concentration was measured in extract liquor after centrifugation. Then, the loaded residue (98.6 mg g^{-1}) was washed with distilled water, 25 mL of 0.1 mol L^{-1} NaCl, 0.1 mol L^{-1} NaOH, 0.1 or 1.0 mol L^{-1} Na_2CO_3 was added and shaken for 1 h and centrifuged. The released IDB concentration (C_R) was measured by UV and the recovery efficiency, E (%), was calculated by Eq. (4).

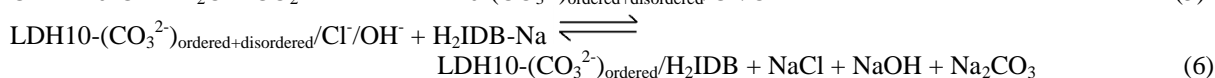
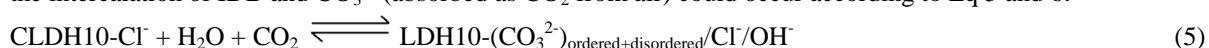
$$E = \frac{C_R}{C_0 - C_f} 100 \text{ (%) } \quad (4)$$

RESULTS AND DISCUSSION

3.1. Effect of initial pH:

Fig. 2 shows the adsorption capacity (q_e) of CLDH10 for IDB after 24 h of equilibration. It slightly ranged between values of $303 - 331 \text{ mg g}^{-1}$ from pH 10.3 to 8.7 at which maximum adsorption capacity was obtained. This may be explained as due to the positive electrical charge of CLDH10 and the anionic nature of IDB at $\text{pH} > 6.1$ [24], electrostatic forces facilitate the adsorption processes. At high pH values > 8.7 , acid sites at the solid surface are neutralized by OH anions coming from the solution, and the amount of sites available to IDB anions decreases so, the adsorbent has maximum adsorption capacity at initial pH value around 8.7. In addition, at high pH, IDB may have increasing competition with OH^- [27]. The final pH rose to 9.7 - 10.5 which indicates the replacement of IDB with $\text{OH}^-/\text{CO}_3^{2-}/\text{Cl}^-$.

This may be confirmed by the appearance of the symmetric and asymmetric sulfonate vibration peak of IDB in the FTIR pattern of the loaded CLDH10 (Fig. 3) at 1047 and 1190 cm^{-1} , respectively [26]. The bands observed at 1367 cm^{-1} in the FTIR pattern of CLDH10 and its loaded form to a lesser extent represent the asymmetric stretching vibration of ordered CO_3^{2-} group; ν_3 [29] which may be trapped from air. Consequently, the intercalation of IDB and CO_3^{2-} (absorbed as CO_2 from air) could occur according to Eq 5 and 6:



3.2. Effect of shaking time:

The effect of shaking time on the adsorption of IDB with initial concentration of 100 mg L^{-1} onto CLDH10 is shown in Fig. 4. The rate of adsorption of IDB was rapid in the early stage but stabilized after 6 h at which

98.6% of IDB was removed. This is largely due to the large active sites on CLDH10 being available at the start of the adsorption process. Eventually, the surface adsorption sites become exhausted where at this point, the limiting rate is the adsorbate transportation from the exterior to the interior sites of the adsorbent particles [27].

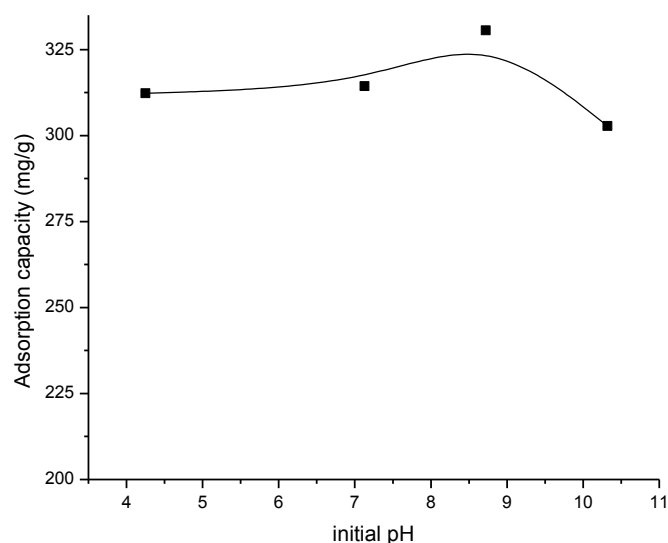


Fig. 2: Effect of initial pH value on the removal efficiency of IDB onto CLDH10.

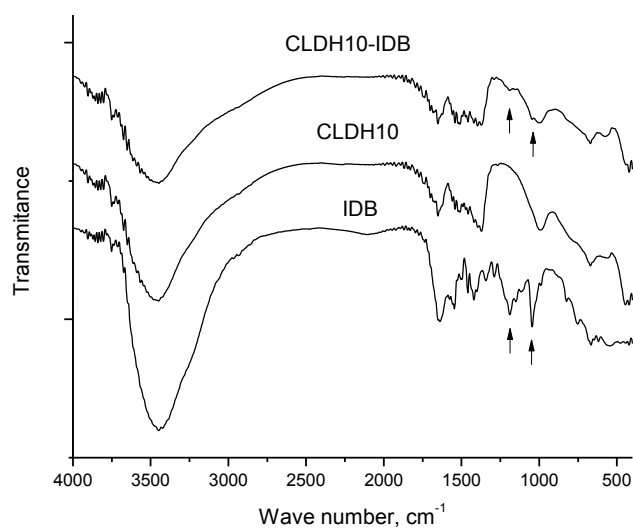


Fig. 3: FTIR spectra of IDB, CLDH10 and CLDH10-IDB.

Adsorption kinetics can be modeled using pseudo-first order and pseudo-second order kinetics models given in literature [28,29]. The linear regression coefficients of the pseudo-second order kinetics model, compared to the pseudo-first order model, for removal of IDB using the layered double hydroxides materials indicates that the experimental data are better described by the pseudo-second-order model for CLDH10 (Table 1), therefore suggesting that the rate is limited by chemisorption. This supposes that the heterogeneous chemisorption mechanism is likely to be responsible for the uptake of IDB ions. The q_e value calculated with this model are close to that determined experimentally. This behavior was independent of the experimental variables, i.e. adsorbent, IDB initial concentration and pH [30]. As expected, the initial adsorption rate was high.

3.3. Effect of initial IDB concentration:

The effect of initial IDB concentration on its adsorption onto 25 mg of CLDH10 at an initial pH 8.7 is shown in Fig. 5. The removal of IDB was dependent on the initial IDB concentration where the removal efficiency (%) decreased with increasing initial IDB concentration. Efficiency of IDB removal was obtained in

the range of 41.9-98.6% using CLDH10 as adsorbent. This may be explained by the exhaustion of the limited active sites on the adsorbent surface, hence increasing the competition amongst IDB species for positively charged groups on the surface of the adsorbent.

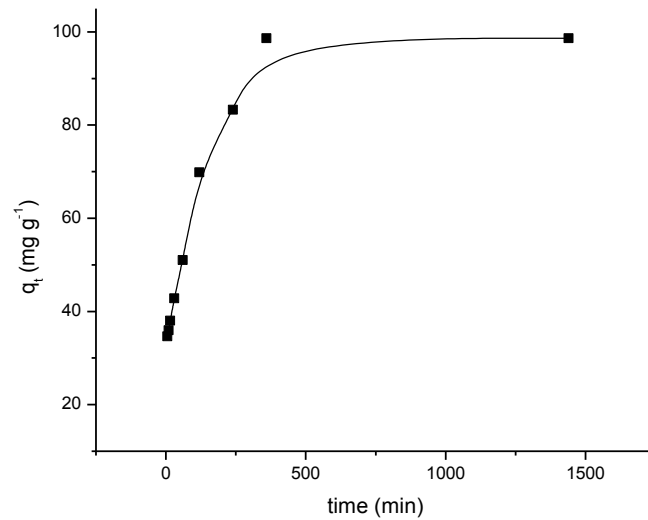


Fig. 4: Effect of shaking time on the adsorption capacity of IDB onto CLDH10 at pH value 8.7.

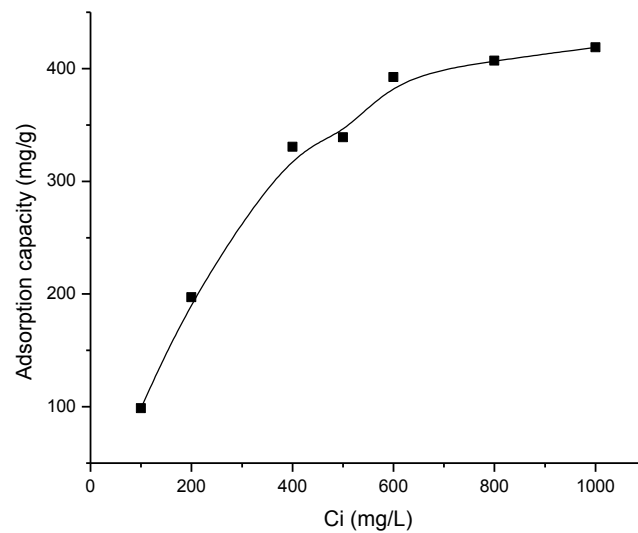


Fig. 5: Effect of the initial concentration on the adsorption capacity of IDB onto CLDH10 at pH 8.7.

Table 1: Kinetic model constants and correlation coefficients for adsorption of IDB onto CLDH10.

C_0 ($mg L^{-1}$)	$q_{e, exp}$ ($mg g^{-1}$)	Pseudo-first order			Pseudo-second order		
		$k_1 \times 10^{-2}$ (min^{-1})	$q_{e, cal}$ ($mg g^{-1}$)	R^2	$k_2 \times 10^{-4}$ ($g mg^{-1} min^{-1}$)	$q_{e, cal}$ ($mg g^{-1}$)	R^2
100	98.6	2.67	15.9	0.587	2.99	100.9	0.998

k_1 is the rate constant of the pseudo-first order adsorption (min^{-1}) and k_2 is the rate constant of pseudo-second order adsorption ($g mg^{-1} min^{-1}$).

The adsorption isotherm models Langmuir and Freundlich were investigated using the data of effect of IDB initial concentration on the adsorption efficiency of CLDH10 as described in literature [31 - 33]. The separation factor R_L indicates the shape of the isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable isotherm ($R_L > 1$). From Table 2, R_L values for IDB ions adsorption were found to vary between 0.014-0.124 which are less than 1. This confirms that CLDH10 is favorable for adsorption of IDB ions from aqueous solution.

Table 2: Langmuir and Freundlich parameters for IDB adsorption onto CLDH10.

q_{exp} $mg\ g^{-1}$	Langmuir parameters				Freundlich parameters		
	q_{cal} $mg\ g^{-1}$	R_L	b $L\ mg^{-1}$	r^2	K_F	$1/n$	r^2
418.9	423.7	0.014- 0.124	0.071	0.997	121.2	0.211	0.8799

C_0 is the initial IDB ions concentration ($mg\ L^{-1}$). q_{max} is the maximum adsorption capacity ($mg\ g^{-1}$). b is the Langmuir adsorption constant ($L\ mg^{-1}$). K_F is a rough indicator of the adsorption capacity and $1/n$ is the adsorption intensity.

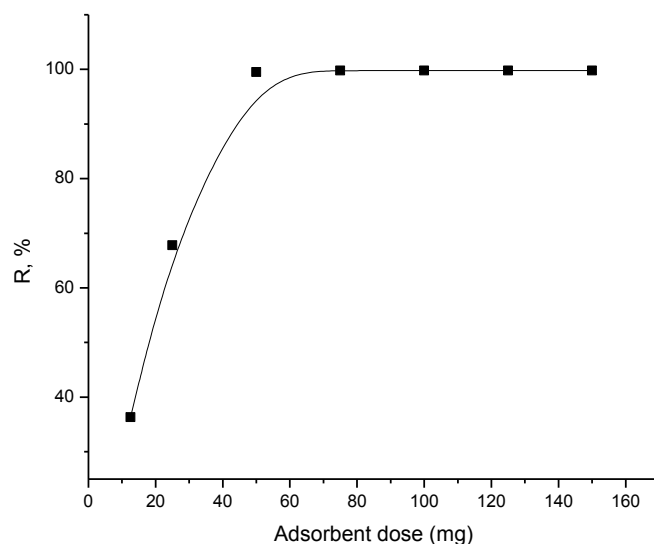
The calculated value of $1/n$ is less than 1 representing favorable adsorption conditions for the removal of IDB ions on CLDH10. The Freundlich parameters for the adsorption of IDB ions are also given in Table 2.

Accordingly, the maximum adsorption capacity, q_{cal} evaluated from Langmuir model was found to be $423.7\ mg\ g^{-1}$, which is close to the experimental value ($418.9\ mg\ g^{-1} \approx 48.7\ mmol$ per 100 g). In addition the fitness of linear form evaluated from two models was examined by regression coefficients (r^2). Consequently, the Langmuir model isotherm can describe the adsorption of IDB ions onto the tested LDH because the r^2 value is 0.997.

A comparison of the present capacity of CLDH10 for IDB adsorption with the adsorption capacities of newly reported CLDHs may confirm its adsorption efficiency. Mg-Zn/Al- CO_3 CLDH adsorbs sulfonated dyes as Astrazon Remazol Brilliant Blue and Direct Red with maximum capacities of 13.1 and 7.38 mmol per 100 g, respectively [6]. Also 2Mg/Al- CO_3 CLDH could adsorb 18 mmol Remazol Golden Yellow per 100 g [34]. So, it may be recognized that CLDH10 has high adsorption capacity and a good kinetics and dosage for IDB removal (> 99%).

3.4. Effect of adsorbent dosage:

An optimum dosage of suitable adsorbent for adsorbate removal in a batch adsorption system is important for its cost-effective application. Complete removal of $500\ mg\ L^{-1}$ of IDB (>99%) was achieved at adsorbent dosage $\geq 50\ mg$ (0.2% w/v) of CLDH10. The removal percentage increased with the increase in adsorbent dose (Fig. 6). The removal percentage increased from 36.3% for adsorbent dose of 0.05% (w/v) to 99.8% removal of IDB at > 0.2 w/v. Increase in IDB removal with adsorbent dose can be attributed to the increased surface area and the availability of more adsorption sites [25].

**Fig. 6:** Effect of adsorbent dose on the removal efficiency of IDB onto CLDH10 at pH value 8.7.

3.5. Release study:

Table 3 shows the release results of IDB-loaded CLDH10 using NaCl, NaOH or Na_2CO_3 with a concentration 0.1 and $1.0\ mol\ L^{-1}$ at room temperature and $50\ ^\circ C$. The order of elution efficiency of IDB from CLDH10 was $Na_2CO_3 > NaOH > NaCl$ (2.01-29.4%), which indicates the relative intercalation preferences of their anions. This was attributed to a high degree of affinity of carbonate for LDH [6,25]. Increasing the applied temperature of batch-mode desorption from room temperature to $50\ ^\circ C$ increased the release of the loaded IDB. Usage of $1\ mol\ L^{-1}\ Na_2CO_3$ increased the single-batch elution efficiency up to 29.4% that indicates the relative bonding of IDB to LDH layers compared with the eluent anions.

Table 3: Release of IDB-loaded CLDH10 with 25 mL of eluents. Ci = 100 mg L⁻¹ and concentration of adsorbed IDB = 86.8 ppm.

Eluent	Concentration of eluent, mol L ⁻¹	Eluted IDB at room temperature		Eluted IDB at 50 °C	
		mg L ⁻¹	%	mg L ⁻¹	mg L ⁻¹
NaCl	0.1	1.99	2.01	4.30	4.36
NaOH	0.1	8.85	8.97	14.6	14.8
Na ₂ CO ₃	0.1	16.6	16.7	22.2	22.5
Na ₂ CO ₃	1.0	23.4	23.7	28.9	29.4

4. Conclusion:

The layered double hydroxide (CO₃)_{0.22}/Cl_{0.55}-Mg_{3.67}Zn_{0.26}Al (CLDH10) was studied as a potential sorbent for IDB. Optimum pH for adsorption was at pH=8.7 and time of shaking 6 h. A pseudo-second order rate kinetics model was suggested for the adsorption process indicating a chemisorption mechanism. Langmuir-type adsorption isotherm model was suggested with a high monolayer capacity of 423.7 mg g⁻¹ higher than reported CLDH adsorbents for sulfonated dyes.

The adsorbed IDB was recovered in a single-batch elution with an efficiency of 29.4%, which confirms that it will not represent a secondary sludge waste upon application for IDB removal.

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