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Enhancing removal of hexavalent chromium using biochar, graphitic carbon nitride (GCN) and ZnFe-LDH from wastewater

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Here we prepared co-pyrolyzed, biochar, GCN and LDH and compared for their hexavalent chromium (Cr(VI)) adsorption capacity. Several factors such as aqueous pH, sorption contact time, metal concentration, sorbent dose and recyclability of the sorbents were investigated to assess the potential of biochar, LDH and GCN. The results showed that the maximum Cr(VI) removal was obtained using LDH (91%) at pH 4.9 followed by GCN and biochar. The effect of contact time on Cr(VI) adsorption by all three sorbents proved that 2 h time was optimum for maximum Cr(VI) sorption. Kinetic modeling showed the better fit of PSO ($R^2 = 0.99$) than PFO while Langmuir model proved to be superior than other isotherm models confirming that Cr(VI) removal mechanism was monolayer sorption process. The FTIR graphs showed that C=N, C–N, OH, $–NH_2$ and M−O groups contributed in Cr(VI) elimination via electrostatic interactions or surface complexation process. The uneven and porous surface of LDH and other sorbents helped in capturing the aqueous Cr(VI) ions from contaminated water. Overall, LDH proved to be more efficient than other sorbents and thus could be successfully applied as single application or by making composites in the treatment of Cr(VI)-containing wastewater.

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1. Introduction

Massive industrialization has led to the discharge of significant amount of pollutants including heavy metals in different segments of the environment causing serious health hazards to humans and other living organisms. The industrial waste contains different kinds of heavy metals such as cadmium (Cd), zinc (Zn), copper (Cu), nickel (Ni), and chromium (Cr) [1]. Among them, Cr is considered as the most toxic heavy metals present in various parts of environment. Chromium occurs mainly from − 2 to + 6 oxidation state while among these states Cr(III) and Cr(VI) are the major stable species which could easily be transported and cause potential health effects [2, 3]. In general, Cr(III) ions has the capability to attach with the organic matter in soil as hydroxides, sulfates and oxides. The Cr(III) is less mobile, soluble and toxic, while Cr(VI) is present as highly soluble and mobile Cr species. Various anthropogenic practices result in the releases of Cr(VI) ions into the water bodies including painting, dyeing, pigment production, tanning, electroplating and food preservation industries [4, 5]. The toxicity of Cr(VI) makes it a teratogen, mutagen and carcinogen [6, 7]. Additionally, Cr(VI) may pose skin diseases, kidney and liver impairment, and lethal lung cancer [8]. In order to protect the environment from toxic Cr(VI), various countries have set maximum allowable limit of Cr(VI) with regard to drinking water . The World Health Organization (WHO) has set a maximum level of Cr as 0.05 mg L^{-1} in drinking water. [9, 10]. Thus, it is necessary to eradicate Cr(VI) from contaminated water for protection and sustainability of our environment.

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Various remediation techniques have been applied to eliminate Cr from contaminated water, however, most of the conventional removal methods are either expensive, less efficient or could lead to the production of secondary wastes [11, 12]. Adsorption is considered as more acceptable and applicable owing to lower maintenance and operational cost as well as easy regeneration/recyclability of sorbents with minimal/no side effects [13, 14]. However, the finding of suitable adsorbent is very important for the successful application of the process. Various materials such as biochar, activated carbon, agriculture-based biosorbents, nano-sized metals, clays, carbon-based nanomaterials and layered double hydroxides (LDHs) were prepared and used to treat heavy metals-contaminated water [15-19].

Biochar is carbon-rich material which is produced through pyrolysis of feedstock material including agriculture waste, sludge, and organic solid wastes. It possesses high surface area, porous structure, long-term stability and abundant functional groups which help in removal of contaminants from contaminated water [20, 21].

Carbon-nitrogen based compounds have been synthesized and gained the attention of the researchers in recent past because of their excellent catalytic, electrical and specifically the adsorption capabilities [22, 23]. Among them, graphitic carbon nitride (GCN) has emerged as a non-toxic, chemically stable, inexpensive material possessing great thermal stability. The GCN possess a planar-conjugated stable structure due to sp^2 bonds of C and N, thus making it highly beneficial for the carrier transmission [24]. The amino groups (NH_2) present on GCN help in quick and precise attachment of toxic metal ions through ion exchange interactions and surface complexation process [25]. Although the photocatalytic potential of GCN has been examined extensively but adsorption performance for Cr(VI) ions has rarely been reported in previous research work.

Layered double hydroxides (LDHs), which are sometimes known as hydrotalcite or multifunctional anionic clays, gained the interests owing to their ecofriendly nature, stability, and efficient adsorption potential for anions in aqueous solution [26, 27]. The LDH has the formula as $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, in which M^{II} shows a divalent metal cation, whereas M^{III} is denoted to trivalent metal cation and A^{n-} depicts interlayer charge compensating anions [28]. The LDHs have already been used to treat various pollutants in soil, for example, Alidokht, et al. [29] prepared nanoscale FeAl-LDHs and successfully reduced leachable toxic Cr(VI) ions to less toxic Cr(III) ions, exhibiting robust and strong reducing abilities. The LDHs have great capability to be applied in wastewater treatment because of their high surface area, stability, easy regeneration and outstanding adsorption potential. For anions such as Cr(VI), LDHs normally adsorb Cr(VI) via ion exchange mechanism as well as intercalation within their layers. Furthermore, there are a huge number of anions, such as carbonate and sulfate in LDH layers, which could be helpful in adsorbing both anionic and cationic heavy metals by precipitation, ion exchange and isomorphous substitution. In the past, researchers have revealed LDHs and their modified compounds for the removal of metallic ions and organic contaminants from aqueous solution [30]. For example, LDHs have shown excellent adsorption potential for uranium (211.58 mg g^{-1}) [31]. The surface induced precipitation, ion exchange and tunability features of LDHs make them excellent candidate for remediation of heavy metals containing wastewater [32].

Therefore, this study was planned with idea to compare the Cr(VI) removal potential of organic-based sorbent (biochar) and inorganic-based sorbents (GCN and LDH). The objectives of the current study were to compare the Cr(VI) adsorption capacity of biochar, GCN and LDH under varying environmental conditions such as pH, time, metal concentration, sorbent dose. The recyclability potential of sorbents was also asses to find out their regeneration potential. The mechanism of Cr(VI) elimination was examined using equilibrium modeling while the surface functional groups, elemental composition and surface morphological features of sorbents were also evaluated.

2. Materials and methods

2.1. Solutions and chemicals

Potassium chromate salt was employed to make the chromium stock solution (1000 mg L^{-1}) while sub-stock solutions (100, 200, mg L^{-1}) were prepared by dilution method. Deionized water (DW) and analytically pure chemicals were used during the experimental work. The $FeSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$, NaOH, potassium chromate, melamine were attained from internationally reputable company (Sigma Aldrich).

2.2. Biochar preparation

Rice husk (RH) was obtained from agriculture farm while sugarcane bagasse (SB) was collected from local sugar producing mill. After that, biowastes were subjected to careful washing with DW to eradicate dust residues and impurities. The biowastes then completely dried in sunlight followed by oven-drying (70 °C) for 24 h. The materials were ground to make uniform size (200 μm) and put in sealed bags for further use. The physicochemical analyses of both raw feedstock materials were evaluated and can be found in our previous study [33].

To prepare biochar, the biowastes were co-pyrolyzed for 120 minutes using pyrolysis unit set at 450 °C temperature (5 °C min^{-1}) while N_2 gas was also supplied. The system was cooled down to achieve normal temperature and the material referred to as biochar now was collected. The prepared biochar was crushed and sieved to make uniform size and stored for future use in the experiments.

2.3. Graphitic Carbon Nitride (GCN)

The GCN ($g\text{-}C_3N_4$) was made by employing melamine. Briefly, 20 g of the required salt was put in a muffle furnace set at 550 °C temperature and residence time was 5 hours. The temperature was increased gradually with 10 °C min^{-1} during the preparation of GCN.

2.4. Layer double hydroxide (LDH)

The ZnFe-LDH was synthesized as follows: 0.08 mol L^{-1} of $ZnSO_4 \cdot 7H_2O$ and 0.04 mol L^{-1} of $FeSO_4 \cdot 7H_2O$ and 1 M NaOH was added drop-wise to deionized water (100 mL). The pH of solution was maintained at around 8 and stirring was done for 1-2 hours. The prepared material was aged for one day at ambient environment. Following the filtration, the LDH particles were collected and washed thoroughly using DW to eradicate extra salts. The final Zn-Fe LDH product was made by oven-drying the solid precipitates for 12 hours at 60 ºC (Figure 3). The prepared biochar, GCN and LDH were applied in the experiments to sorb Cr(VI) from water under diverse environmental conditions.

2.5. Sorption Experiments

2.5.1. pH

The pH was tested from 3-8 with contact time 2 hours, optimum sorbent dose and initial Cr(VI) concentration of 100 mg L^{-1}. After agitating the solution for 2 hours, centrifugation was done followed by filtration. The Cr was analyzed in the solution using atomic absorption spectrometer.

2.5.2. Contact Time

In this experiment, the contact time ranged 1-240 mins with optimum sorbent dose, 100 mg L^{-1} Cr(VI) and optimum pH value obtained from pH study. The sorption samples were filtered, centrifuged and used for Cr determination.

2.5.3. Initial Cr Concentration

Initial Cr(VI) concentration of 1-200 mg L^{-1} was applied for this study with optimum sorbent dose, contact time of 2 hours and the optimal solution pH value. The solution mixture was preserved and used to analyze Cr.

2.5.4. Sorbent Dose

In this study, the sorbent dose was ranged 0.4–2.4 g L^{-1} with contact time of 2 hours, optimal solution pH value and Cr(VI) concentration same as in pH study. After shaking the sorption solution for 2 hours, centrifugation was done followed by filtration to determine Cr.

The Cr elimination from wastewater expressed in percentage was attained using Equation 1:

$$Cr\ removal\ (\%)\ =\ \frac{C_o\ -\ C_e}{C_o}\times 100 \tag{1}$$

here, C_o and C_e show initial and final metal concentrations expressed as mg L^{-1}, respectively. The Cr sorption capacity (q_e) of sorbents was evaluated by applying below given formula (Equation 2):

$$q_e(\ mgg^{-1})\ =\ \frac{(C_o\ -\ C_e)\ V}{m} \tag{2}$$

where, m and V demonstrate sorbent weight (g) and volume of sorption working system in L.

2.5.5. Recyclability/regeneration of Sorbents

For this purpose, NaOH (0.1 M) was applied in 3 consecutive regeneration steps. In each cycle, the sorbents after Cr treatment were put in NaOH solution and agitated for 30 mins at room temperature and solution mixture was subjected to Cr analyses.

2.6. Solid Phase Analyses

The fourier transform infrared (FTIR) spectroscopy technique was applied to identify surface functional groups. The surface structure and elemental constituents of all three sorbents were revealed by using scanning electron microscopy attached with energy dispersive X-ray (SEM-EDS) spectroscopy.

2.7. Sorption Modeling, Quality control and Quality assurance

The data from sorption experiments was computed in kinetic and isotherm modeling using Sigma Plot and Microsoft Excel (2010) [33]. All the glassware was thoroughly cleaned by employing HNO_3 (2%) and DW during all the experiments. The precision/accuracy was checked by the analysis of spiked Cr samples solution (2-10 mg L^{-1}).

3. Results and discussion

3.1. Analysis of solid phase

3.1.1. FTIR

The identification of major surface functional groups on the surface of biochar, GCN and LDH was made using FTIR analyses (Figure 1).

For co-pyrolyzed biochar, the surface functional groups ranged from 400–4000 cm^{-1}. The Figure 1a demonstrates FTIR spectra of raw biochar and Cr(VI) loaded biochar in which peaks at 3751 and 3298 cm^{-1} of raw biochar highlights the occurrence of –OH stretching of a few macromolecules having pectin, lignin, and cellulose [34, 35]. Similarly, at 2919 and 2851 cm^{-1} of raw biochar, the vibration of C–H stretching indicated the participation of some alkyl functional moieties having methylene, methoxy and methyl groups [36]. At wave numbers 1582, 1511, 1437, 1375 cm^{-1} of raw biochar demonstrated carboxylic (COO–) groups with hemicellulose, protein, pectin and surface functional moieties [37]. The band at 800 cm^{-1} of raw biochar surface is probably denoted to extending stretching –NH_2 functional groups thus indicating their presence on raw biochar applied here [37, 38].

After Cr(VI) loading, the shifting of peaks to 3754 and 3348 cm^{-1}, respectively illustrating active participation of –OH groups in Cr(VI) sorption via complexation mechanism. While shifted peaks at 2920 could be reported to alkyl functional groups participation in the sorption process [39]. Similarly, the change of peaks at 1592, 1438, 1368 cm^{-1} might be assigned to contribution of carboxylic functional groups (COO–) in the Cr(VI) loading by surface complexation interactions between Cr(VI) and COO– [40]. The $–NH_2$ functional groups involvement was also established by shift of band at 721 cm^{-1} after Cr(VI) removal from water which was owing to electrostatic interactions between Cr(VI) and $–NH_2$ groups probably. Overall, three major functional groups for instance carboxylic, amine and hydroxyl were involved in sorption by raw biochar.

In case of GCN, Figure 1b represents the typical bands at 730 cm^{-1} which illustrated typical peaks of triazine units, specifically indicating graphitic characteristics of GCN. The intense bands within 1128-1623 cm^{-1} ascribed to C=N as well as C–N stretching, specifically associated with nitrogen-rich tri-s-triazine of GCN [41]. The peaks of aromatic-based C–N group in the structure of GCN are demonstrated at 1538 , 1390, 1311 cm^{-1} [42].

The Cr(VI)-loaded GCN illustrated that the peaks at 730, 1128, 1311, 1390 and 1538 were shifted to 729, 1224, 1312, 1391 and 1537 cm^{-1}, respectively exhibiting the assistance of aforementioned moieties in Cr(VI) adsorption. Generally, GCN shows the contribution of carbonyl and nitrogen-based functional groups during Cr(VI) adsorption through complexation mechanism [43, 44].

For LDH, FTIR spectra confirmed that band located at 721 cm^{-1} was denoted to M−O groups where M represents Fe or Zn (Figure 1c) [45, 46]. Moreover, vibrations at 1081 cm^{-1} were due to C–O bands of ester and while the peak at 1265 cm^{-1} might be correspond to the alcohol groups vibrations (O–H) [47, 48].

Moreover, the transmittance broad peak area found between 3,300–3,800 cm^{-1} were assigned to the O–H vibrations which appeared from metal-hydroxide functional groups as well as interlayer water molecules in ZnFe-LDH [49, 50].

After Cr(VI) loading specific peaks at 721, 1081, 1265 and 3248 cm^{-1} were transferred to 658, 1034, 1110 and 3269 cm^{-1}, respectively which showed their active involvement for Cr(VI) removal. Furthermore, these shifts in peaks showed the significant contribution of abovementioned groups particularly M−O based groups for Cr(VI) removal [51].

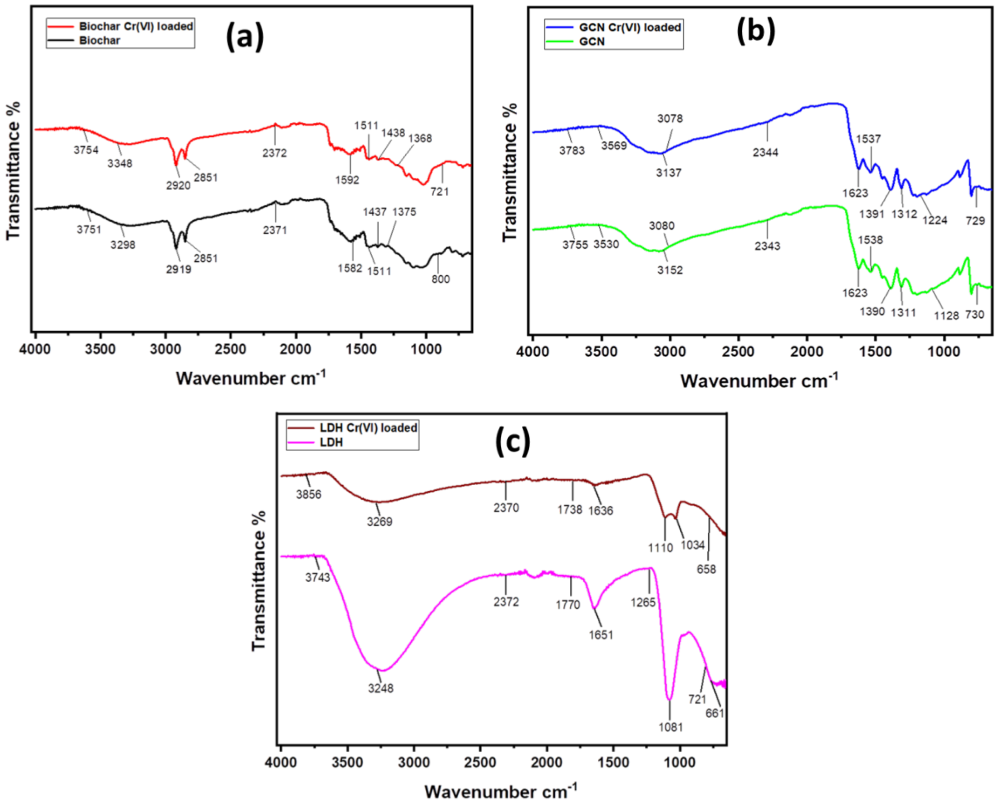


Fig. 1. FTIR of biochar (a), GCN (b) and LDH (c) before and after successfully adsorbing Cr(VI).

3.1.2. SEM-EDS

To know about the surface morphology of sorbents SEM analysis was performed. The SEM micrograph of biochar is depicted in Figure 2a which confirmed formation of pores in the biochar surface which is due to release of volatile matter from feedstock materials after pyrolysis was done. This was also related to the residence time of feedstock during pyrolysis temperature [52].

Biochar surface was reported as rough and uneven, containing numerous micropores and macropores of various shapes which certainly could offer useful sorption cavities and sites during sorption of pollutants such as Cr(VI). These distinct and abundant pores can efficiently capture Cr(VI) and other toxins from water [53].

The SEM micrographs of GCN revealed a layered types structure in which bulk sheet-like shape similar to the graphite (Figure 2b) was noted. This structure provided a shape in which thick sheets were stacked on other sheets [44]. Moreover, the GCN surface showed unequal lamellar shape and agglomerated as the cluster. This irregular structure of GCN might offer various cavities for pollutants adsorption [41]. The SEM micrographs of LDH exhibited small irregular shaped flakes, sheet like structure with irregular agglomerates having various pores owing to uniform dispersion of the LDH (Figure 2c) [54]. This uneven and porous structure of LDH might be useful in removal of Cr(VI).

The elemental compositions of all three sorbents were noted in the EDS spectra, as shown in Figure 3a-c. The EDS spectra of biochar indicated the presence of C (55.88%), N (11.69%), O (28.16%), K (2.92%) and other elements (Figure 3a-c).

Similarly, GCN showed the occurrence of C (25%), N (56.41%), O (10.13%) and other elements while the EDS spectra of LDH revealed that Zn (34.97%) and Fe (28.25%) were the major elements in addition to C (3.21%), N (3.28%), O (17.64%) and other elements in LDH structure. The occurrence of these elements in all sorbents was useful in the sorption of pollutants (Cr) from water.

3.2. pH

The sorption system pH is reportedly a major factor in sorption of toxins including Cr(VI) because It can significantly interfere with the surface charge of materials as well as different form of Cr(VI) [55]. Thus, in this experiment, LDH, GCN and biochar application for Cr(VI) sorption proved to be linked with pH and increased at the start from 3 to 4.93 pH but afterwards a rapid decline was observed in sorption with the pH value from 5–9 (Figure 4a,b). The LDH yielded maximum sorption (91%; 56.88 mg g^{-1}) with pH 4.9 followed by GCN (84.27%; 52.67 mg g^{-1}) with pH 4.83 and biochar (82.16%; 51.35 mg g^{-1}) at 4.93 pH. The removal efficacy was largely related to solution pH and maximum efficiency obtained at pH value 4.9 by LDH compared to other sorbents. It was obvious that solution pH controls the movement of Cr(VI) ions and also controls the suitable charge existing on sorbent for sorption.

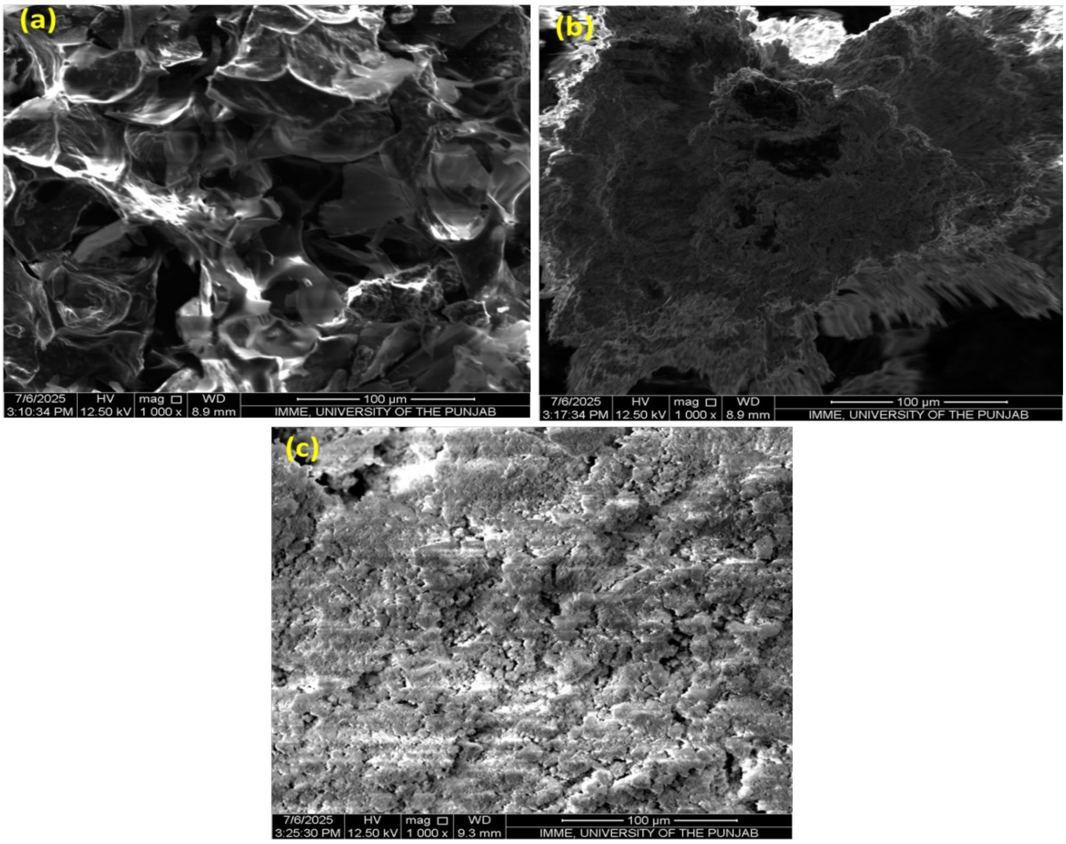
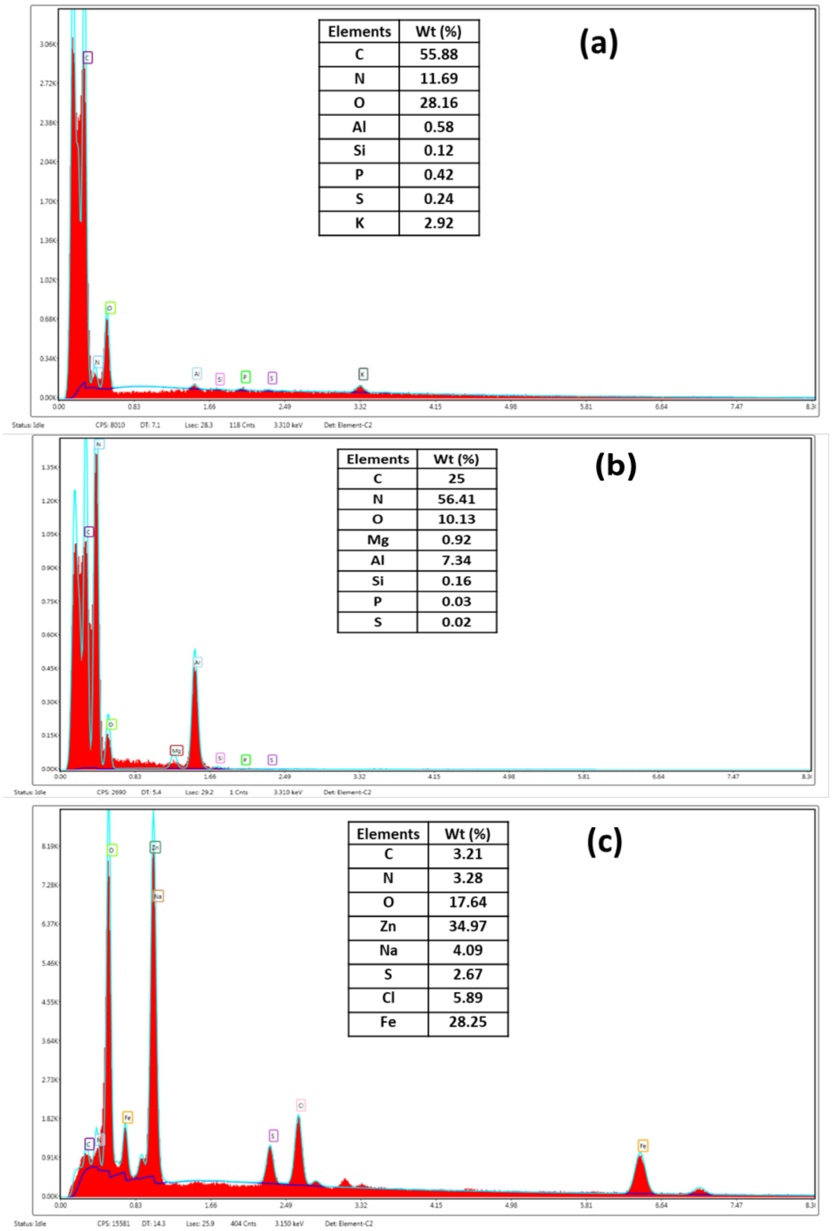


Fig. 2. The SEM micrographs of three sorbents; biochar (a), GCN (b) LDH (c).

The alteration in removal potential at the varying pH levels by LDH could be due to the strong attraction of LDH surface for various Cr species present in the pH range of this study [56, 57]. It is documented that LDH-based materials usually have positive surface charge because of the existence of OH_2^+, that probably assists in electrostatic reaction [58]. Around 2-6 pH, the Cr species are present as CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$ in water environment. At pH > 7, the main Cr species exist as CrO_4^{2-} [59, 60]. Here, Cr(VI) species were present largely as CrO_4^{2-} and $HCrO_4^-$ at pH ~4.9 and thus highly positively charged surface of LDH strongly attracted negatively charged Cr species owing to electrostatic attraction [61, 62]. At pH level 2-4, species of Cr(VI) were present as $HCrO_4^-$ and hence less removal was observed which was largely attributed to low electrostatic attractive forces between LDH and Cr(VI) resulting in less sorption at low pH.



(a)

Elements	Wt (%)
C	55.88
N	11.69
O	28.16
Al	0.58
Si	0.12
P	0.42
S	0.24
K	2.92

(b)

Elements	Wt (%)
C	25
N	56.41
O	10.13
Mg	0.92
Al	7.34
Si	0.16
P	0.03
S	0.02

(c)

Elements	Wt (%)
C	3.21
N	3.28
O	17.64
Zn	34.97
Na	4.09
S	2.67
Cl	5.89
Fe	28.25

Fig. 3. EDS analysis of three sorbents; biochar (a), GCN (b) and LDH (c).

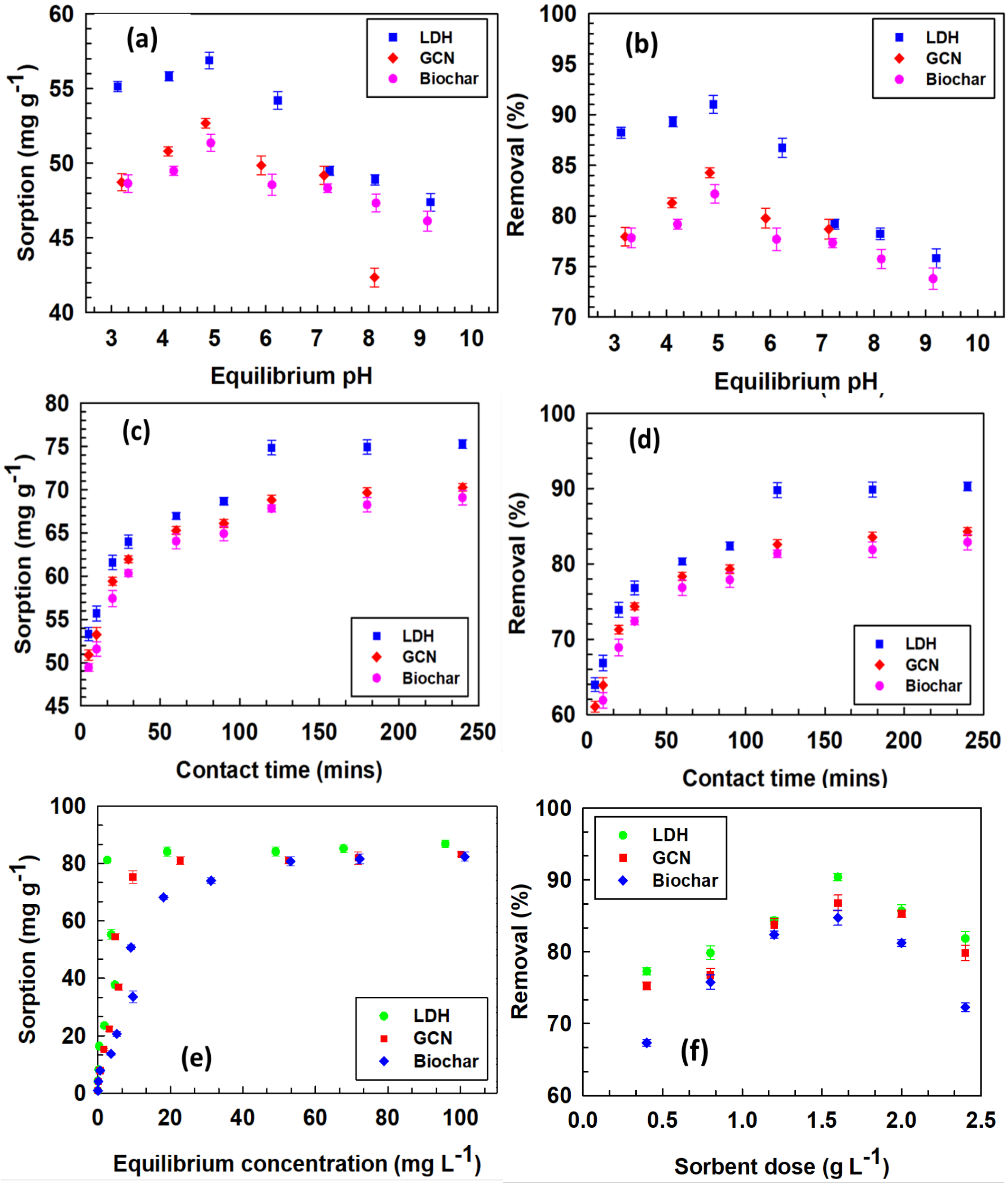


Fig. 4. The influence of varying pH (a, b), contact time (c,d), initial concentration (e) and sorbent dose (f) using three sorbents.

3.3. Contact Time

To find out the efficient reaction time for highest adsorption of Cr(VI) using biochar, GCN and LDH, the influence of adsorption time was examined (Figure 4c,d). It is indicated that the quick increase in adsorption potential within 120 mins (2h) was because of large quantity of adsorption sites on all three sorbents, which indicated a strong association between Cr(VI) ions and sorbents applied. The highest adsorption was provided by LDH (74.83 mg g^{-1}, 89.80 %) followed by GCN (68.8 mg g^{-1}, 82.56 %) and biochar (67.82 mg g^{-1}, 81.38 %) at equilibrium time of 2h. This is probably because of occurrence of enough useful sorption cavities at the start of reaction, leading to diffusion of Cr(VI) ions inside the micropores of sorbents [63, 64]. However, afterwards, raising the reaction time provided less influence and thus the process of sorption slowed down (>2h), confirming that active sites were saturated rapidly in initial 2 h of time [65]. Hence, prolonged reaction time of sorption either halted Cr(VI) removal or caused release of already sorbed ions from the surface of studied sorbents in sorption working solution [66, 67].

3.4. Initial Concentration

The effect of metal concentration has significant effect on effectiveness of sorbents as represented in Figure 4e. The results from experiment clearly explained that raising the Cr(VI) concentration provided a rapid sorption rate owing to significance concentration gradient hence causing high shifting of Cr(VI) ions from solution phase to all sorbents [68, 69]. When the system achieved equilibrium at 100-150 mg L^{-1} level, additional increment in Cr(VI) led to decreased sorption rate due to less number of active sorption sites thereby causing reduced sorption at equilibrium [70, 71].

3.5. Sorbent Dose

The change in sorbent dose significantly affected Cr(VI) removal rate and it was increased when sorbent dose was enhanced gradually (0.4-1.6 g L^{-1}) (Figure 4f). This indicated the presence of a large number of active sorption sites thereby causing a rapid Cr(VI) adsorption [72]. However, more rise in sorbent dose resulted in a declined removal because the amount of ions (Cr) was same in the sorption solution.

Moreover, the excessive increase sorbent dosage resulted in decreasing sorption potential of Cr(VI) which proposed that amount of adsorbent above the certain level could not be efficiently use. The excess sorbent dose probably results in the polymerization and agglomeration between adsorbent thus significantly decreased the Cr(VI) removal and led to wastage of sorbents [73, 74]. Hence, 1.6 g L^{-1} dosage provided 90.38, 86.78 and 84.73% removal by LDH, GCN and biochar, respectively.

3.6. Adsorption Kinetic Models

The kinetic data from sorption experiments was computed into pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models and results are presented in Figures 5a-f and Table 1. As observed in Table 1, R^2 values of PSO kinetics were greater as compared to PFO kinetics, which suggested that Cr(VI) adsorption was well-explained by PSO model, and further strengthened chemically reactive nature of sorption process. Moreover, the value of q_e calculated from PSO model for all three sorbents found to be more close to the original experimental data. The kinetic modeling results indicated that Cr(VI) adsorption mechanism onto biochar, GCN and LDH was complex and adsorption was probably due to external mass transfer across macropores of sorbets as well as internal diffusion trough micropores [75]. Moreover, chemisorption process might also be responsible for Cr(VI) sorption since the Cr(VI ions could make complexes surface functional groups of sorbents [76, 77].

3.7. Sorption isotherm models

To explore sorption process and sorption mechanism, four isotherm models were used on isotherm equilibrium results [78]. The data from models demonstrated that Langmuir showed higher R^2 values ranging from 0.96-0.85 than Freundlich while fitting curves obtained from Langmuir model were more close to original experimental data. (Figures 6a-c; Table 2). Hence, the results assume that surface of sorbent is homogeneous, and sorption happened in a single layer (monolayer). Furthermore, Q_L data obtained from Langmuir model was found to be 7.73 (biochar), 17.09 (GCN), 39.92 (LDH) mg g^{-1}, respectively, suggesting the superior sorption potential of LDH than other sorbents.

Moreover, Temkin model provided higher R^2 (0.81) for using LDH than those of GCN (0.78) and biochar (0.77) (Figures 6a-c; Table 2). The value of b which is known as heat of sorption was observed as 11.21, 11.47 and 11.25 by biochar, GCN and LDH (Table 2). This proposed that a linear reduction in the amount of b provided greater dispersion of ions onto the sorbents [79]. Moreover, in this study, Dubinin-Redushkevich (D-R) model showed the R^2 ranged 0.95-0.81 for Cr(VI) sorption on all three sorbents (Figure 6a-c ; Table 2). Here, the E values (which is the bonding energy) found to be 0.01-0.02 kJ g^{-1} (Table 2) which suggests that physical sorption might also occur for Cr(VI) [80]. But extremely low E values which were very much less than 8-16 kJ g^{-1} optimum range proposed that here D-R model was unfit to unravel adsorption mechanism/process [81, 82].

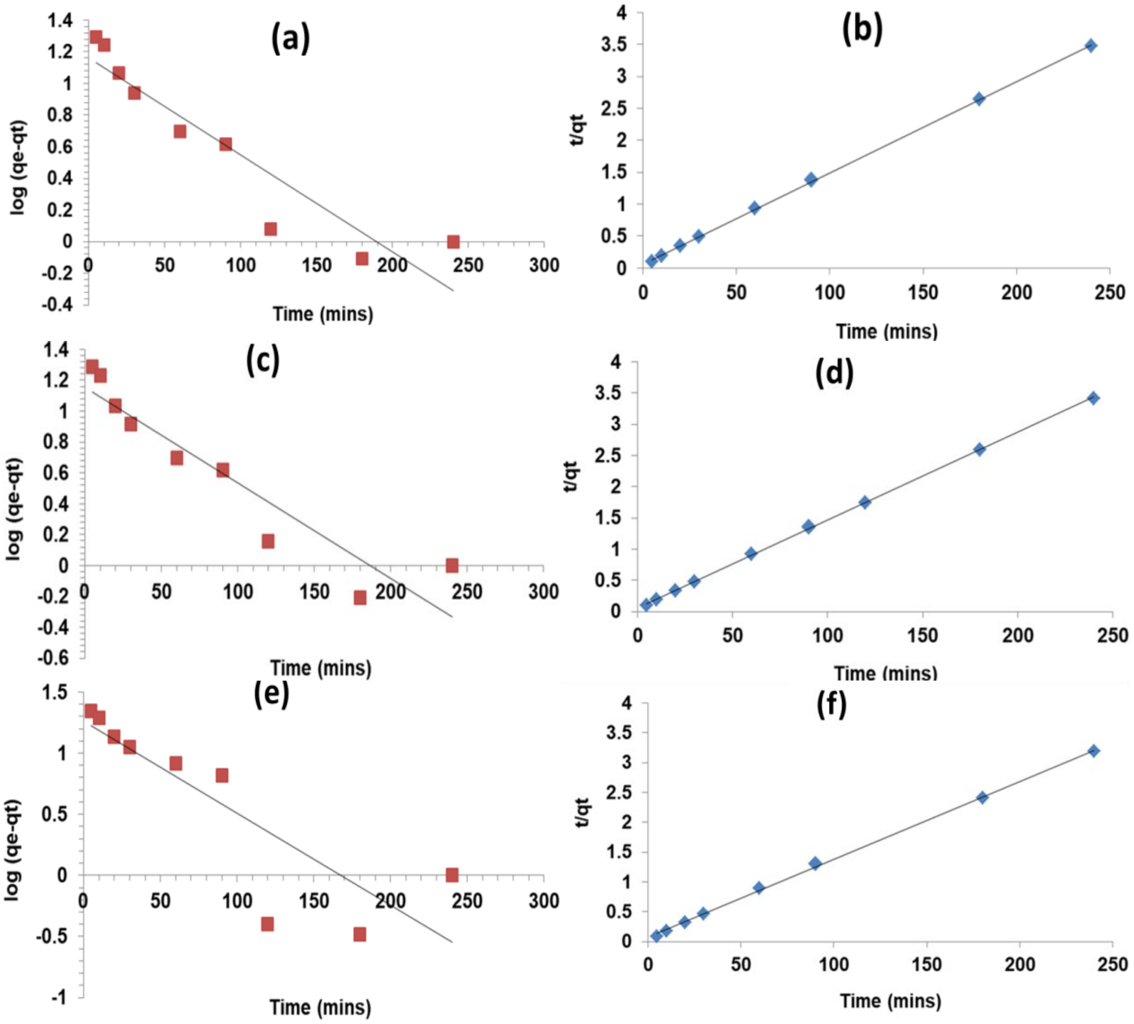


Fig. 5. Kinetic models graph of biochar (a,b), GCN (c,d) and LDH (e,f) data obtained by applying (a,c,e) PFO and (b,d,f) PSO.

Table 1. Kinetic model constants calculation for Cr(VI) sorption on sorbents.

Model	Parameters	Values	*Unit*	*R^2*
Biochar				
Pseudo-first-order kinetic model	$q_{e\ \mathrm{cal}}$	14.45	mg g^{-1}	0.87
	k_1	0.01	min^{-1}	
Pseudo-second-order kinetic model	$q_{e\ \mathrm{cal}}$	71.43	mg g^{-1}	0.99
	k_1	0.014	g mg^{-1} min^{-1}	
GCN				
Pseudo-first-order kinetic model	$q_{e\ \mathrm{cal}}$	14.12	mg g^{-1}	0.88
	k_1	0.01	min^{-1}	
Pseudo-second-order kinetic model	$q_{e\ \mathrm{cal}}$	70.92	mg g^{-1}	0.99
	k_1	0.014	g mg^{-1} min^{-1}	
LDH				
Pseudo-first-order kinetic model	$q_{e\ \mathrm{cal}}$	18.28	mg g^{-1}	0.93
	k_1	0.01	min^{-1}	
Pseudo-second-order kinetic model	$q_{e\ \mathrm{cal}}$	76.33	mg g^{-1}	0.99
	k_1	0.013	g mg^{-1} min^{-1}	

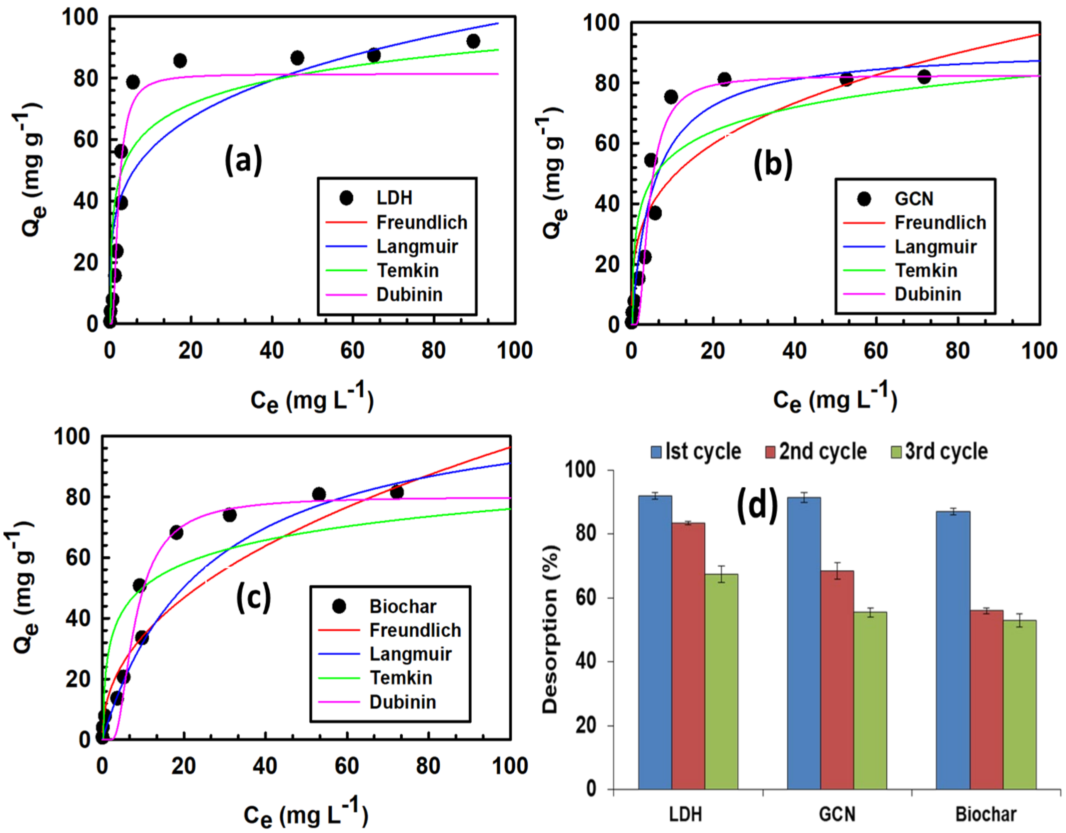


Fig. 6. Isotherm modeling for LDH (a), GCN, (b) and biochar (c) data; recyclability study (d).

Table 2. Modeling parameters results extracted from equilibrium data for all three sorbents.

Model	Parameter	Unit	Sorbent		
			Biochar	GCN	LDH
Freundlich	*n*	-	0.39	0.29	0.24
	Q_F	(mg^{1-n} g^{-1} L^{n})	17.18	24.78	32.54
	R^2	-	0.88	0.81	0.76
Langmuir	K_L	(L g^{-1})	0.07	0.18	0.45
	Q_L	(mg g^{-1})	7.73	17.09	39.92
	R^2		0.96	0.93	0.85
Temkin	*A*	-	8.76	13.12	28.62
	b	-	11.21	11.47	11.25
	R^2	-	0.77	0.78	0.81
D-R	*E*	(kJ g^{-1})	0.02	0.01	0.01
	Q_d	(mg g^{-1})	80.07	82.38	81.26
	R^2		0.95	0.94	0.81

3.8. Recyclability/regeneration

The ability of sorbents to be reusable, regenerative and economical is very important in order to have successful water treatment system. Recycled/regenerated materials offer cost-effective solution as well as possibility of recovering of valuable resources. Here, LDH showed significant reusability potential of upto 67.5% than GCN (55.5%) and biochar (53%) in 3 sorption/desorption cycles (Figure 6d). In 1st cycle, Cr(VI) desorption was obtained as 92% (LDH), 91.5% (GCN) and 87% (biochar). The regeneration efficiency of sorbents reduced when centrifugation was done and resulted in decreased desorption potential in 2nd and 3rd cycles. However, in comparison, even after the 3rd cycle, the LDH sustained a high desorption efficiency than GCN and biochar thus showing that it could be an efficient candidate for real-world applications in water treatment system.

4. Conclusions

It was concluded that, LDH provided the highest Cr(VI) removal (91%) at pH 4.9 with the 2 h contact time and Cr concentration (100 mg L^{-1}). Kinetic and isotherm modeling data illustrated the dominance of PSO kinetics ($R^2 = 0.99$) and Langmuir model with R^2 values of up to 0.96, respectively. Hence, it was confirmed that the sorption mechanism for C(VI) was a single layer process. The porous and rough surface of LDH and other sorbents in addition to carbonyl, –OH, $–NH_2$ and M−O groups assisted in eliminating Cr(VI) via electrostatic reactions or surface complexation process. The LDH-based sorbents could be significantly capable in eliminating Cr(VI) from polluted water. Moreover, in future research, LDH-based materials could be combined with other organic and inorganic materials to make composites which could further improve the system of Cr(VI) and other heavy metals treatment.

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References

[1] K. Jomova, S.Y. Alomar, E. Nepovimova, K. Kuca, M. Valko, Archives of toxicology, 99, 153, (2025); https://doi.org/10.1007/s00204-024-03903-2

[2] M.A. Irshad, S. Sattar, R. Nawaz, S.A. Al-Hussain, M. Rizwan, A. Bukhari, M. Waseem, A. Irfan, A. Inam, M.E. Zaki, Ecotoxicology and environmental safety, 263, 115231, (2023); https://doi.org/10.1016/j.ecoenv.2023.115231

[3] M.-N. Georgaki, M. Charalambous, N. Kazakis, M.A. Talias, C. Georgakis, T. Papamitsou, C. Mytiglaki, Environments, 10, 33, (2023); https://doi.org/10.3390/environments10020033

[4] Z. Bao, H. Feng, W. Tu, L. Li, Q. Li, Environmental Science and Pollution Research, 29, 35501, (2022); https://doi.org/10.1007/s11356-022-19452-z

[5] S. Zha, A. Yu, Z. Wang, Q. Shi, X. Cheng, C. Liu, C. Deng, G. Zeng, S. Luo, Z. Zhao, Chemical Engineering Journal, 489, 151457, (2024); https://doi.org/10.1016/j.cej.2024.151457

[6] E. Sazakli, International Journal of Environmental Research and Public Health, 21, 406, (2024); https://doi.org/10.3390/ijerph21040406

[7] H. Guo, C. Liu, S. Yan, J. Yin, J. Shan, Journal of Hydrology, 638, 131480, (2024); https://doi.org/10.1016/j.jhydrol.2024.131480

[8] S. Xie, Green Chemistry Letters and Reviews, 17, 2356614, (2024); https://doi.org/10.1080/17518253.2024.2357213

[9] IARC, (1990).

[10] IARC, (2012).

[11] T. Shao, Q. Yin, J. Bai, J. Zhu, M. Gan, Environmental Research, 266, 120449, (2025); https://doi.org/10.1016/j.envres.2024.120449

[12] N. Hassan, A. Jalil, M. Bahari, N. Izzuddin, N. Fauzi, N. Jusoh, M. Kamaroddin, R. Saravanan, H. Tehubijuluw, Environmental Research, 259, 119584, (2024); https://doi.org/10.1016/j.envres.2024.119584

[13] K.H.H. Aziz, F.S. Mustafa, R.F. Hamarawf, K.M. Omer, Journal of Water Process Engineering, 70, 106867, (2025); https://doi.org/10.1016/j.jwpe.2024.106867

[14] J. Bayuo, M.J. Rwiza, J.W. Choi, K.M. Mtei, A. Hosseini-Bandegharaei, M. Sillanpää, Advances in Colloid and Interface Science, 329, 103196, (2024); https://doi.org/10.1016/j.cis.2024.103196

[15] W.A. Al-Amrani, S.A. Onaizi, Separation and Purification Technology, 343, 127018, (2024); https://doi.org/10.1016/j.seppur.2024.127018

[16] Z. Raji, A. Karim, A. Karam, S. Khalloufi, Waste, MDPI, 2023, p. 775-805; https://doi.org/10.3390/waste1030046

[17] T. He, Q. Li, T. Lin, J. Li, S. Bai, S. An, X. Kong, Y.-F. Song, Chemical Engineering Journal, 462, 142041, (2023); https://doi.org/10.1016/j.cej.2023.142041

[18] A. Kłos, S. Wierzba, M. Piechaczek-Wereszczyńska, K. Matik, M. Głowacki, M. Płotka, A. Gawdzik, M. Wiatkowski, A. Dołhańczuk-Śródka, Z. Ziembik, Scientific Reports, 15, 5088, (2025); https://doi.org/10.1038/s41598-025-89365-7

[19] A. Reda, A.-G. El-Demerdash, W. Sadik, E. El-Rafey, T. Shoeib, Applied Water Science, 15, 25, (2025); https://doi.org/10.1007/s13201-024-02343-8

[20] M. Afshar, S. Mofatteh, Results in Engineering, 23, 102433, (2024); https://doi.org/10.1016/j.rineng.2024.102433

[21] K.H.H. Aziz, Desalination and Water Treatment, 320, 100757, (2024); https://doi.org/10.1016/j.dwt.2024.100757

[22] J.R. Koduru, L.P. Lingamdinne, C.A. Pal, Y.-L. Choi, R. Kulkarni, Z.H. Momin, Y.-Y. Chang, Journal of Water Process Engineering, 57, 104610, (2024); https://doi.org/10.1016/j.jwpe.2023.104610

[23] O.A. Oyewo, Chemistry Africa, 7, 391, (2024); https://doi.org/10.1007/s42250-023-00768-3

[24] S. Patnaik, S. Martha, G. Madras, K. Parida, Physical Chemistry Chemical Physics, 18, 28502, (2016); https://doi.org/10.1039/C6CP04262G

[25] J. Guo, T. Chen, X. Zhou, T. Zheng, W. Xia, C. Zhong, Y. Liu, Applied Organometallic Chemistry, 33, (2019); https://doi.org/10.1002/aoc.5119

[26] S. Zhao, Z. Meng, X. Fan, R. Jing, J. Yang, Y. Shao, X. Liu, M. Wu, Q. Zhang, A. Liu, Chemical Engineering Journal, 390, 124554, (2020); https://doi.org/10.1016/j.cej.2020.124554

[27] S. Zhao, Z. Li, H. Wang, H. Huang, C. Xia, D. Liang, J. Yang, Q. Zhang, Z. Meng, Separation and Purification Technology, 263, 118419, (2021); https://doi.org/10.1016/j.seppur.2021.118419

[28] S. Zhao, M. Wu, R. Jing, X. Liu, Y. Shao, Q. Zhang, F. Lv, A. Liu, Z. Meng, Applied Clay Science, 182, 105297, (2019); https://doi.org/10.1016/j.clay.2019.105297

[29] L. Alidokht, S. Oustan, A. Khataee, M.R. Neyshabouri, A. Reyhanitabar, Geoderma, 380, 114648, (2020); https://doi.org/10.1016/j.geoderma.2020.114648

[30] M. Hu, D. Zhao, X. Yan, Y. Wang, J. Zhang, X. Hu, M. Zhou, P. Liu, Applied Catalysis B: Environment and Energy, 362, 124753, (2025); https://doi.org/10.1016/j.apcatb.2024.124753

[31] P. Wang, L. Yin, X. Wang, G. Zhao, S. Yu, G. Song, J. Xie, A. Alsaedi, T. Hayat, X. Wang, Journal of Environmental Management, 217, 468, (2018); https://doi.org/10.1016/j.jenvman.2018.03.112

[32] L. Luo, C. Hou, L. Wang, W. Zhang, C. Wang, J. Liu, Y. Wu, C. Wang, Catalysts, 14, 252,

(2024); https://doi.org/10.3390/catal14040252

[33] F. Sharif, S. Ali, M. Zahid, M. Adrees, M.S. Arif, Journal of Molecular Liquids, 429, 127582, (2025); https://doi.org/10.1016/j.molliq.2025.127582

[34] H. Qiu, L. Lv, B.-c. Pan, Q.-j. Zhang, W.-m. Zhang, Q.-x. Zhang, Journal of Zhejiang University-Science A, 10, 716, (2009); https://doi.org/10.1631/jzus.A0820524

[35] S.S. Kalaivani, T. Vidhyadevi, A. Murugesan, K.V. Thiruvengadaravi, D. Anuradha, S. Sivanesan, L. Ravikumar, Water Resources and Industry, 5, 21, (2014); https://doi.org/10.1016/j.wri.2014.04.001

[36] M.B. Shakoor, U. Khalil, S. Ali, F. Sharif, S.R. Ahmad, M. Rizwan, A. Jilani, K.A. Al-Ghanim, P.K. Sarker, Environmental Pollutants and Bioavailability, 36, 2368590, (2024); https://doi.org/10.1080/26395940.2024.2368590

[37] U. Khalil, M.B. Shakoor, S. Ali, M. Rizwan, M.N. Alyemeni, L. Wijaya, Journal of Saudi Chemical Society, 24, 799, (2020); https://doi.org/10.1016/j.jscs.2020.07.001

[38] M.A. El-Nemr, U.O. Aigbe, M.A. Hassaan, K.E. Ukhurebor, S. Ragab, R.B. Onyancha, O.A. Osibote, A. El Nemr, Biomass Conversion and Biorefinery, 14, 1975, (2024); https://doi.org/10.1007/s13399-022-02327-1

[39] S.O. Owalude, A.C. Tella, Beni-suef university journal of basic and applied sciences, 5, 377, (2016); https://doi.org/10.1016/j.bjbas.2016.11.005

[40] D.B. Pal, A. Singh, J.M. Jha, N. Srivastava, A. Hashem, M.A. Alakeel, E.F. Abd_Allah, V.K. Gupta, Bioresource Technology, 339, 125606, (2021); https://doi.org/10.1016/j.biortech.2021.125606

[41] A.H. Warda, M. Rostom, M.I. Mashaly, E.T. Helmy, E.A. Gomaa, E.M. AbouElleef, Surfaces and Interfaces, 107123, (2025); https://doi.org/10.1016/j.surfin.2025.107123

[42] Q. Xu, B. Cheng, J. Yu, G. Liu, Carbon, 118, 241, (2017); https://doi.org/10.1016/j.carbon.2017.03.052

[43] Z.H. Momin, L.P. Lingamdinne, R. Kulkarni, C.A.K. Pal, Y.-L. Choi, J.R. Koduru, Y.-Y. Chang, Chemosphere, 346, 140551, (2024); https://doi.org/10.1016/j.chemosphere.2023.140551

[44] P. Attri, M. Chauhan, R. Singh, S. Kumar, P. Garg, D.-K. Lim, G.R. Chaudhary, Chemosphere, 364, 143178, (2024); https://doi.org/10.1016/j.chemosphere.2024.143178

[45] S. Dowlatshah, M. Saraji, M. Dinari, R. Soltani, Journal of Separation Science, 44, 2972, (2021); https://doi.org/10.1002/jssc.202001245

[46] Z. Zhang, C. Liu, H. Cai, Z. Liu, C. Xiao, Separation Science and Technology, 60, 761, (2025); https://doi.org/10.1080/01496395.2025.2455966

[47] G. Lartey-Young, L. Ma, Chemosphere, 293, 133526, (2022); https://doi.org/10.1016/j.chemosphere.2022.133526

[48] M.P. Barman, H. Saikia, Inorganic Chemistry Communications, 178, 114521, (2025); https://doi.org/10.1016/j.inoche.2025.114521

[49] N. Ayawei, A. Ekubo, D. Wankasi, E. Dikio, European Journal of Scientific Research, 130, 235, (2015).

[50] M. Shi, Z. Zhou, Q. Li, Q. Liao, W. Yang, M. Si, Z. Yang, Q. Wang, Journal of Hazardous Materials, 480, 136459, (2024); https://doi.org/10.1016/j.jhazmat.2024.136459

[51] H.M. Elshishini, G.M. Elsubruiti, Z.F. Ghatass, A.S. Eltaweil, Journal of Solid State Chemistry, 335, 124689, (2024); https://doi.org/10.1016/j.jssc.2024.124689

[52] N. Hossain, S. Nizamuddin, G. Griffin, P. Selvakannan, N.M. Mubarak, T.M.I. Mahlia, Scientific reports, 10, 18851, (2020); https://doi.org/10.1038/s41598-020-75936-3

[53] Y. Tan, J. Wang, L. Zhan, H. Yang, Y. Gong, Scientific Reports, 14, 4853, (2024); https://doi.org/10.1038/s41598-024-55520-9

[54] E. Abdel-Hady, S.H. Hafez, H.F. Mohamed, M.R. Elsharkawy, Scientific Reports, 14, 16501,

(2024); https://doi.org/10.1038/s41598-024-65889-2

[55] J. Gao, X. Zhang, J. Bai, X. Li, C. Wang, J. Cheng, Z. Xu, X. Jin, Journal of Water Process Engineering, 61, 105331, (2024); https://doi.org/10.1016/j.jwpe.2024.105331

[56] M. Avila, T. Burks, F. Akhtar, M. Göthelid, P.C. Lansåker, M.S. Toprak, M. Muhammed, A. Uheida, Chemical Engineering Journal, 245, 201, (2014); https://doi.org/10.1016/j.cej.2014.02.034

[57] R. Khalili, M.M. Sabzehmeidani, M. Parvinnia, M. Ghaedi, Environmental Nanotechnology, Monitoring & Management, 18, 100750, (2022); https://doi.org/10.1016/j.enmm.2022.100750

[58] S.S. Nemati, G. Dehghan, A. Khataee, L. Alidokht, N. Kudaibergenov, Journal of Environmental Chemical Engineering, 12, 114742, (2024); https://doi.org/10.1016/j.jece.2024.114742

[59] B. Zhang, L. Luan, R. Gao, F. Li, Y. Li, T. Wu, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 520, 399, (2017); https://doi.org/10.1016/j.colsurfa.2017.01.074

[60] M.E. Mahmoud, S.M. Elsayed, S.E.M.E. Mahmoud, R.O. Aljedaani, M.A. Salam, Journal of Molecular Liquids, 347, 118274, (2022); https://doi.org/10.1016/j.molliq.2021.118274

[61] J. Bell, X. Ma, T.J. McDonald, C.-H. Huang, V.K. Sharma, ACS ES&T Water, 2, 932, (2022); https://doi.org/10.1021/acsestwater.1c00409

[62] W. Usmani, M.A. Inam, R. Iftikhar, I. Irfan, R. Adnan, M.B.K. Niazi, R. Khan, M. Hassan, Journal of Water Process Engineering, 55, 104233, (2023); https://doi.org/10.1016/j.jwpe.2023.104233

[63] R. Zein, J.S. Purnomo, P. Ramadhani, M.F. Alif, C.N. Putri, Arabian Journal of Chemistry, 16, 104480, (2023); https://doi.org/10.1016/j.arabjc.2022.104480

[64] W. Youssef, A. Hussein, M. Taha, M. El-Maadawy, Russian Journal of Inorganic Chemistry, 67, 1058, (2022); https://doi.org/10.1134/S0036023622070245

[65] K. Li, Z. Liu, T. Wen, L. Chen, Y. Dong, Journal of Radioanalytical and Nuclear Chemistry, 292, 269, (2012); https://doi.org/10.1007/s10967-011-1400-8

[66] F. Cai, F. Ma, X. Zhang, P. Reimus, L. Qi, Y. Wang, D. Lu, H.V. Thanh, Z. Dai, Science of the Total Environment, 900, 165819, (2023); https://doi.org/10.1016/j.scitotenv.2023.165819

[67] O.P. Murphy, M. Vashishtha, P. Palanisamy, K.V. Kumar, ACS omega, 8, 17407, (2023); https://doi.org/10.1021/acsomega.2c08155

[68] C. Ruan, G. Chen, Y. Ma, C. Du, C. He, X. Liu, X. Jin, Q. Chen, S. He, Y. Huang, Journal of Colloid and Interface Science, 630, 544, (2023); https://doi.org/10.1016/j.jcis.2022.10.020

[69] S. Charazińska, E. Burszta-Adamiak, P. Lochyński, Reviews in Environmental Science and Bio/Technology, 21, 105, (2022); https://doi.org/10.1007/s11157-021-09599-5

[70] X. Guo, J. Wang, Journal of Hazardous Materials, 402, 123709, (2021); https://doi.org/10.1016/j.jhazmat.2020.123709

[71] A. Abd-Elhamid, E.A. Elgoud, H. Aly, Cellulose, 29, 6231, (2022); https://doi.org/10.1007/s10570-022-04656-w

[72] Đ. Katnić, S.J. Porobić, T. Lazarević-Pašti, M. Kojić, T. Tasić, M. Marinović-Cincović, D. Živojinović, Journal of Water Process Engineering, 56, 104487, (2023); https://doi.org/10.1016/j.jwpe.2023.104487

[73] M.A. Mahmoud, A.M. Tayeb, A.M. Daher, O.Y. Bakather, M. Hassan, M.A. Eldoma, Y.A. Elsheikh, A.F. Abouatiaa, Chemical Data Collections, 41, 100896, (2022); https://doi.org/10.1016/j.cdc.2022.100896

[74] Y. Li, Y. Wei, S. Huang, X. Liu, Z. Jin, M. Zhang, J. Qu, Y. Jin, Journal of Molecular Liquids, 269, 824, (2018); https://doi.org/10.1016/j.molliq.2018.08.060

[75] H. Lu, W. Zhang, Y. Yang, X. Huang, S. Wang, R. Qiu, Water Research, 46, 854, (2012); https://doi.org/10.1016/j.watres.2011.11.058

[76] F. Almomani, R.R. Bhosale, Science of the Total Environment, 755, 142654, (2021);

https://doi.org/10.1016/j.scitotenv.2020.142654

[77] M. Musah, Y. Azeh, J. Mathew, M. Umar, Z. Abdulhamid, A. Muhammad, Caliphate Journal of Science and Technology, 4, 20, (2022); https://doi.org/10.4314/cajost.v4i1.3

[78] A.M. Aljeboree, A.F. Alkaim, S.A. Hussein, M. Abed Jawad, I. Hasan, S.A. Khuder, Case Studies in Chemical and Environmental Engineering, 10, 100831, (2024); https://doi.org/10.1016/j.cscee.2024.100831

[79] M.B. Shakoor, N.K. Niazi, I. Bibi, M. Shahid, Z.A. Saqib, M.F. Nawaz, S.M. Shaheen, H. Wang, D.C. Tsang, J. Bundschuh, Environment international, 123, 567, (2019); https://doi.org/10.1016/j.envint.2018.12.049

[80] G. Yuan, J. Kapelewska, K.H. Chu, Chemical Engineering Communications, 1, (2025).

[81] E. Rosales, J. Meijide, T. Tavares, M. Pazos, M. Sanromán, Process Safety and Environmental Protection, 101, 61, (2016); https://doi.org/10.1016/j.psep.2016.03.006

[82] M. Brdar, M. Šćiban, A. Takači, T. Došenović, Chemical Engineering Journal, 183, 108, (2012); https://doi.org/10.1016/j.cej.2011.12.036