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A novel method for synthesis of functionalized hybrids and their application for wastewater treatment

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ABSTRACT

Industrial bloom has emerged to meet the human needs. However, industrial releases have become a major concern and risk to human health. The present investigation is directed at the synthesis of glucose–alumina hybrids using two precursors: conventional and greener standard chemical and spent foil, respectively, following sol–gel synthesis. Each synthesized hybrid was characterized using Fourier transform infra red spectroscopy, scanning electron microscopy, and EDX techniques. The significant contribution of synthesized hybrids is toward remediation of metals (Pb and Cr) from aqueous media. Frequencies at –OH (3,487–3,504 cm^{-1}), C–H (2,935–2,964 cm^{-1}), Al–O (798–800 cm^{-1}), Al–O–C (1,380–1,383 cm^{-1}), and Al–O–Al (659–669 cm^{-1}) indicate that metal cations bind to surface of hybrid through these linkages. Mesoporous structure with narrow distribution (26–40 nm) and significant mass percentage of C, Al, and O is characterized on SEM–EDX. Batch experiments resulted in significantly higher removal of Pb (88%) than Cr (58%) that might be attributed to higher molecular weight of earlier. Further, divalent cation (Pb) provides more chelation for charge transfer with hydroxyl group on hybrids surface. Equilibrium studies are in good agreement with Freundlich and pseudo-second-order kinetics for adsorption process. Study concludes the efficiency of glucose–alumina hybrids from the greener and conventional routes is comparable. The study proposes a model for sustainable wastewater management.

Keywords: Hybrid; Alumina; Glucose; Adsorption; Lead (Pb); Chromium (Cr)

1. Introduction

The rapid and growing industrialization has led to excessive disposal of metals from the major industrial sources like tanneries, petroleum, smelting, mining, pesticides, battery, paint, and pigment manufacturing [1]. These metals due to non-biodegradability and accumulation are known to cause serious diseases and disorders in living systems, even at low concentrations. The toxicities are quite evident and reported in various research articles [2–4]. Removal of metals from wastewaters is considered as one of the most

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important and challenging areas of water treatments for subsequent safe disposal. In the last few years, different treatment techniques have been used [5,6]. These techniques seem to be uneconomical due to high cost, have multisteps, production of residues/sludge due to addition of chemicals whose disposal is another issue. However, the quest for efficient and effective techniques for the removal of metals is still explored. The development of adsorption process as a well-known separation, efficient, and economical methods owing to simple, low maintenance cost, high efficiency, and ease of operation [7] is established. Alumina is an important industrial chemical and successful adsorbent owing to its unique porosity, thermal and mechanical stability, high surface area, and surface acidity/basicity [8,9]. It has also been employed as an inorganic moiety for the synthesis of hybrid materials with 2-mercaptonicotinic acid [10], thiosemicarbazide [11], 1-nitroso-2-naphthol-3, 6-disulfonate [12], dithizone [13], and purpurogallin [14].

The present study is designed for the synthesis of functionalized alumina hybrid using two different precursors: one is greener (spent aluminum foil) and other is conventional (standard chemical salt). This design is in compliance to environmental policies intending at the reduction of waste generation and to save natural resources. Very few studies focused on the use of waste material for different applications [15–17]. Another significant approach of sustainable development is also perceived in the present investigation by applying the synthesized low cost hybrid materials as adsorbents to deal with environmental challenges of metal pollution.

2. Material and methods

2.1. Synthesis of glucose–alumina hybrids

Glucose–alumina hybrids were synthesized from two precursors; conventional and greener employs standard chemical salt (aluminum nitrate) and spent aluminum foil as inorganic moiety and glucose used as organic moiety, following simple sol–gel method reported by Sharma et al. [18] and Kumar et al. [19]. The schematic layout is presented in Fig. 1.

Both inorganic (spent aluminum foil/aluminum nitrate) and organic moiety (glucose) taken as (1:1) into mixture, stirred, and pH was adjusted to 7.5 using NaOH. A gel formed upon aging for 16 h, filtered, oven dried and calcined at 400°C for 2 h. Synthesized hybrids were coded as conventional (HC) and greener precursor (HG). Each glucose–alumina hybrid was characterized by standardized techniques [Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy coupled with electron dispersion (SEM–EDX)] for structural, morphological, and compositional study.

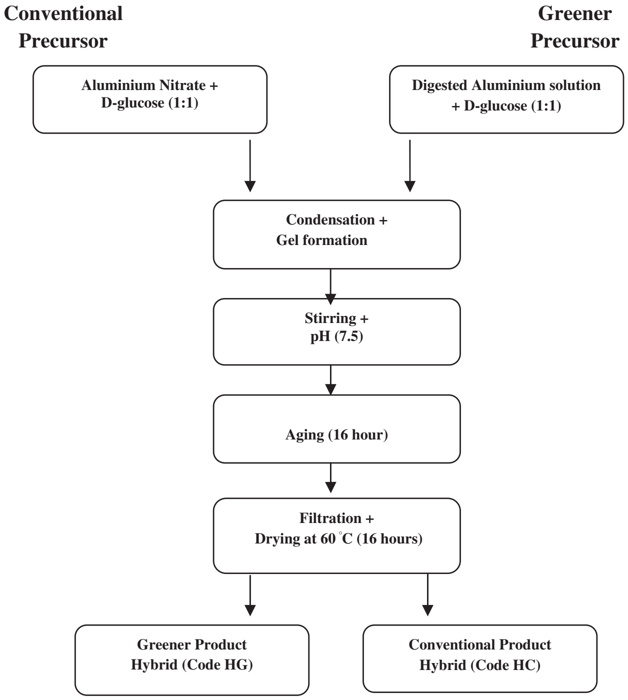

Fig. 1. Schematic layout for the synthesis of alumina-based hybrids.

To identify the main functional groups present on the surface of the adsorbent FTIR spectrophotometer was used (FTIR-8400 Shimadzu, Japan) which was scanned in the range from 4,000 to 400 cm^{-1}.

The morphology and chemical composition of adsorbent was analyzed by SEM and Energy dispersive X-ray (EDX) micrograph obtained from SEM–EDX (Jeol, JSM-6490, Japan).

2.2. Batch adsorption experiment

Each glucose–alumina hybrid was applied as adsorbent for removal of metals (Pb and Cr) in an independent batch experiment as a function of time. A known concentration of both metals was pipetted out into a series of cultural vials containing 5 mg of each synthesized hybrid (as adsorbent). At regular intervals of contact time (in minutes) between adsorbent and adsorbate, the solution was filtered. An aliquot was run on standardized flame atomic absorption spectroscopy (*AA* 200, Varian Inc, Australia) using respective hollow cathode lamps to determine the amount of pollutant adsorbed per unit mass of the adsorbent. The percentage removal was calculated using this equation:

$$\%R = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where R = removal; C_i and C_f = initial and final concentration (mg/l) in solution.

2.3. Kinetic models and isotherms

Different kinetic models [first-order Eq. (2), pseudo-first-order Eq. (3), pseudo-second-order Eq. (4) and intraparticle diffusion Eq. (5)] and isotherms [Langmuir Eq. (6) and Freundlich Eq. (7)] were also applied in order to investigate the fitness of experimental data with predicted one. The value of correlation coefficient (R^2) showed the conformity between experimental data with predicted models values (close or equal to 1). Linear equations of Kinetic models and isotherms are as:

$$\log C_t = \frac{K_1}{2.303} t + \log C_o \tag{2}$$

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k^2 {q_e}^2} + \frac{t}{q_e} \tag{4}$$

$$\log R = \log K_{id} + \log t \tag{5}$$

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_0C_e} \tag{6}$$

$$\log q_e = \log K_f + (1/n) \log C_e \tag{7}$$

3. Results and discussion

The present investigation is centered on the green route synthesis of alumina-based hybrids in comparison with conventional route. The application is envisaged for the adsorptive removal of toxic metals (Pb and Cr). The following modification is carried on reported synthesis protocol which layouts as:

1. Spent aluminum foil (green synthesis) is used in present work for the extraction of alumina as inorganic source for glucose–alumina hybrid synthesis. It provided an economical, sustainable, and greener approach to synthesis in comparison to application of expensive and toxic chemicals (metal salts and organic solvents).
2. Glucose is used as an organic moiety for hybrid synthesis due to non-hazardous, readily available, water soluble instead of using expensive metal alkoxide. Thus, it is attributed as cost-effective and eco-friendly.

3.1. Characterization

3.1.1. FTIR spectroscopy

FTIR analysis (Table 1) showed that broad absorption bands at 3,504 and 3,487 cm^{-1} and at 1,647 cm^{-1} are assigned to stretching and bending vibrations of H–OH. It is due to the presence of adsorbed water in the lattice of synthesized alumina hybrid. Same frequency band was also noted by Saikia [20] and Srivastava et al. [21].

The small and less intense band at 2,964 and 2,935 cm^{-1} assigned to the C–H stretching vibration [20] is due to the presence of glucose. The peak observed at 2,362–2,359 cm and 1,261 cm^{-1} is attributed to the stretching and bending vibration of C–O due to adsorbed carbon dioxide [22] from atmosphere. It is expected as synthesis of alumina hybrids was undertaken at ambient temperature and pressure. The synthesis of hybrid (alumina:glucose) is verified by the sharp and intense bands at 1,386 and 1,383 cm^{-1}, 1,095 and 1,093 cm^{-1} assigned to hybridization of alumina (Al–O^{-}) with aldehyde group of organic moiety (O–CH) and (–C=O) forming Al–O–CH as reported by [Boumaza et al. [23] and Khosla et al. [24]. Further probing of absorption band at 1,022–1,020 cm^{-1} indicates bending mode of Al–(OH), whereas the characteristic peak of main aluminum oxide [25] appears in the region 1,200–400 cm^{-1}. Coordination of alumina matrix (Al–O–Al) in AlO_6 [23] reflects absorption band at 802–785 cm^{-1}.

Table 1
Important FTIR Frequencies of glucose–alumina hybrids

Conventional route (HC) (cm^{-1})	Green route (HG) (cm^{-1})	Assignment	Literature cited
3,487	3,504	O–H (str)	[20,21]
2,935	2,964	C–H (str)	[20]
2,359	2,362	C–O (str)	[22]
1,647	1,647	O–H (b)	[21]
1,383	1,386	Al–O–C (str)	[23]
1,261	1,261	C–O (b)	[24]
798	800	Al–O–Al (AlO_4)	[23]

3.1.2. Scanning electron microscopy

Micrographs of scanning electron microscopy (SEM) showed that hybrids synthesized from greener precursor are irregular shaped blocks with small coarse particles dispersed on surface indicates the presence of carbon/glucose in alumina matrix. Small crevices and holes can also be seen that are expected to participate in adsorption process (Fig. 2).

The particle size assessed from micrograph ranges from 33 to 40 nm. The narrow distribution of particle size in the nanoscale suggests successful conversion of the spent foil (greener inorganic precursor) into the hybrid with organic precursor (glucose). This is also supported by the FTIR analysis showing a linkage of Al–O–C (see Table 1). Narrow distribution is also reported by Meng et al. [26] for mesoporous polymer and homologous carbon framework. Green synthesis is also compared with conventional method for change in morphology.

No remarkable differences are observed. However, particle size (26–40 nm) on average also falls in the same range. The synthesized hybrids may be conveniently regarded as mesoporous with inter-connected semi-ordered pore structure.

3.1.3. Energy dispersive X-ray spectroscopy

It can be seen that aluminum, oxygen, and carbon are the major elements identified in EDX scans (see Fig. 3), encouraging to note that a significant amount of aluminum is present confirming the successful synthesis of glucose–alumina hybrids. On the contrary, aluminum to oxygen ratio shows no significant variation in either of the synthesized hybrids.

3.2. Batch experiment

Time-dependent batch experiments were conducted to determine the removal efficiency of glucose–alumina hybrids toward toxic metals (chromium and lead). Each batch experiment was conducted at known adsorbate concentration (50 mg/l) and adsorbent dose (5 mg) as a function of time till equilibrium is attained. For each observation, minimum of 2 min was provided for adsorbate to adsorbent contact. The results are graphically presented in Figs. 4 and 5.

3.2.1. Adsorption of lead (Pb)

The results showed that the hybrids synthesized from conventional precursor are effective in removing of lead (88%) as a function of time. It is also noted that adsorption increases with increase in time. However, the rate of adsorption is relatively high at initial stages. It might be due to available of active sites [27] followed by slower degree with increasing time. Similar trends in adsorption for other metals are observed by researchers [28,29].

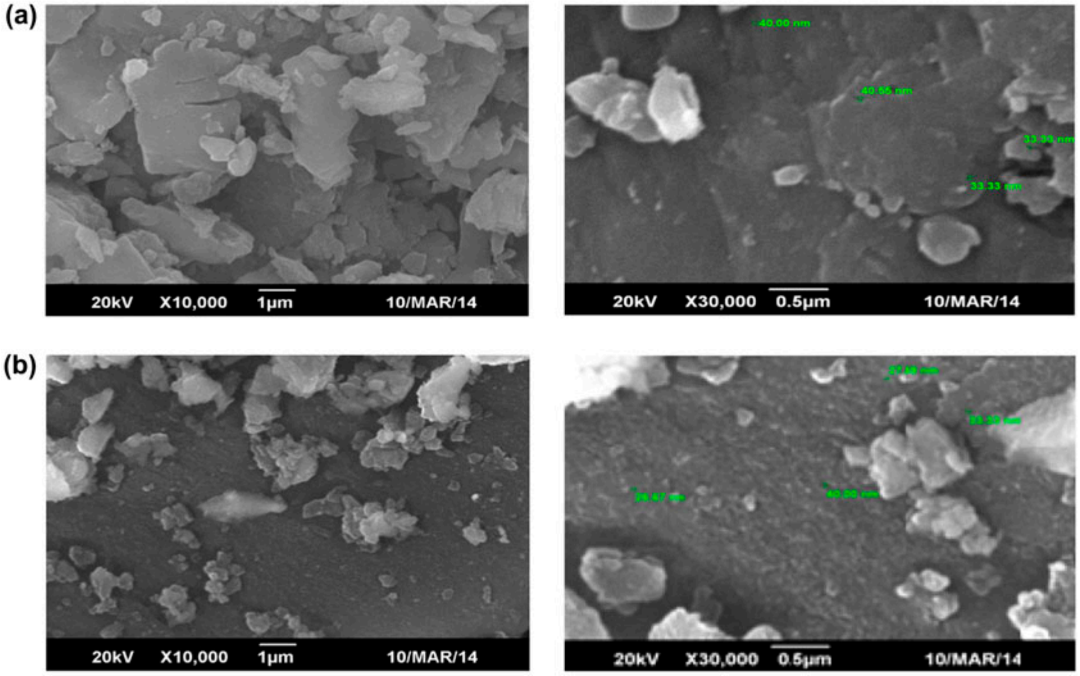

Fig. 2. SEM micrograph of alumina-based hybrids using greener (a = HG) and conventional (b = HC) precursor.

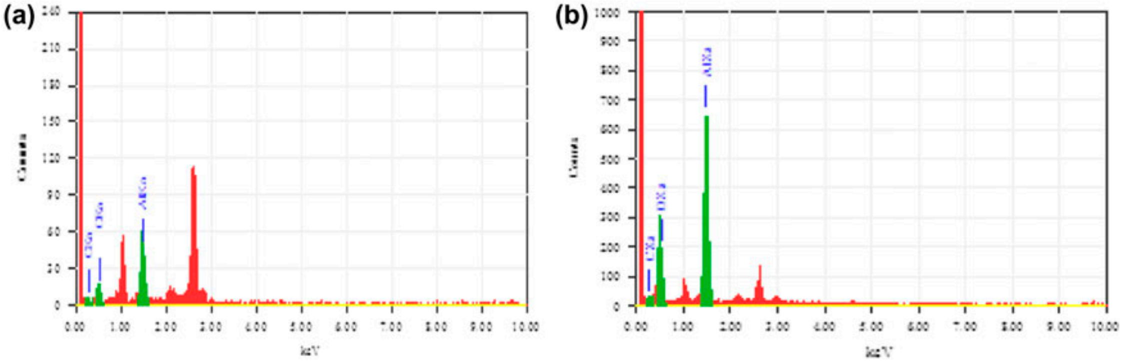

Fig. 3. EDX pattern of alumina-based hybrids using greener (a = HG) and conventional (b = HC) precursor.

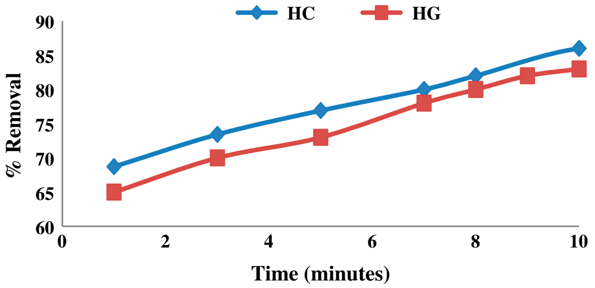

Fig. 4. Percentage removal of lead (Pb) using glucose–alumina hybrids synthesized from conventional (HC) and greener (HG) precursor.

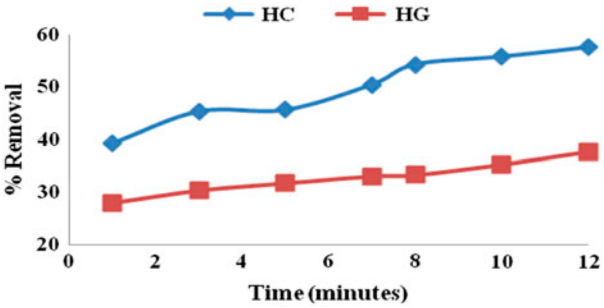

Fig. 5. Percentage removal of chromium using glucose–alumina hybrid from conventional (HC) and greener (HG) precursor.

Commercial activated carbon also behaves similarly for Pb [30]. On the other hand, mercapto-functionalized nano-alumina was applied as adsorbent by Manoochehri et al. [31] for the removal of neodymium and initial rapid removal rates were observed. It is evident from Fig. 4 that equilibrium is attained upon contact of adsorbate with adsorbent in 10–12 min. It suggests that the synthesized adsorbents are effective and efficient in removing Pb from aqueous media. Our adsorbent can be regarded comparably efficient with dithizone-modified alumina for the extraction of 75% Pb within 5 min [14]. Greener route is also adapted for the synthesis of glucose–alumina hybrid showed appreciable good (83%) adsorption capacity.

3.2.2. *Adsorption of chromium (Cr)*

Another metal selected for adsorption studies is chromium. The results are presented in figures. It can be seen that a low uptake capacity (58%) is attained for glucose–alumina hybrid (HC). Further, this uptake shows increasing trend with time until the attainment of equilibrium [32]. The relatively lower optimal removal reported by Akhtar et al. [33] may be attributed to different nature of adsorbate. Activated alumina adsorbed the Cr(III) through ion exchange mechanism studied by Deravanesiyan et al. [34].

The present adsorption mechanism is proposed to develop as a result of physical forces of attraction developing shallow adsorption well at relatively larger distances. Glucose–alumina hybrid synthesized from greener precursor showed 38% chromium removal. Each of the synthesized glucose–alumina hybrids was subjected to adsorption batch. Further, this uptake shows increasing trend with time until the attainment of equilibrium. Low chromium adsorption is also reported by Dal Bosco et al. [35].

3.3. *Comparative analysis*

Comparative analysis of adsorption of Chromium and Lead onto the glucose–alumina hybrids synthesized from conventional and greener precursor (see Fig. 6) shows that Cr(III) is less adsorbed than Pb(II). Adsorption of cations is dependent on many factors including ionic radii, hydration energy,

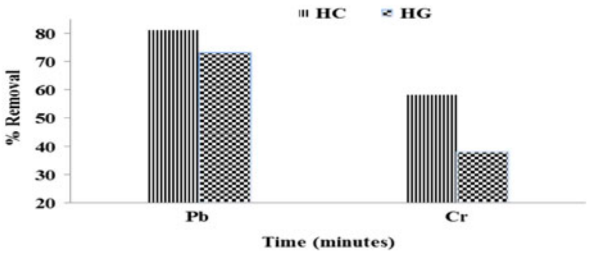

Fig. 6. Comparative analysis of adsorption of metals onto glucose–alumina hybrids using conventional (HC) and greener (HG) precursor.

electronegativity, ionic mobility, and charge density. In the present study, significantly higher percentage removal is noted for Pb may directly be related to higher molecular weight (207) in comparison to Cr (52) contributing more ionization potential to adsorb on the surface. Similarly, Pb^{2+} has higher ionic radii (0.132 nm) than Cr^{3+} (0.061 nm), low hydration energy(−1,481 kJ/mole) than Cr^{3+} (−4,563 kJ/mol) and high electronegativity (1.8) than Cr (1.6). All these factors when combined may be responsible for preferred lead adsorption. Such preferential uptake of lead has also been observed by Rao et al. [36].

Furthermore, the divalent lead (Pb) cation provides more chelation for charge transfer (ionic mobility) with hydroxyl group on hybrid surface in comparison to chromium. Having high ionic charge, low ionic radii, and electronegativity charge density chromium favors more retention than lead, that is why maximum sorption capacity was not achieved [35].

3.4. Proposed mechanism of adsorption

The glucose–alumina hybrids synthesized from two different precursors are applied as adsorbents. The surfaces occupy unique position in exhibiting hydroxyl and oxide groups imparting negative charge. The development of negatively charged surface is likely to contribute in attracting positively charged ion (metal cations) through electrostatic force of attraction resulting in adsorption.

The variation in degree and rate of adsorption depends on whether complexation (chemisorption) or

Table 2
Plot of pseudo-second-order kinetics of lead (Pb) and chromium (Cr) using glucose–alumina hybrids from conventional (HC) and greener (HG) precursor at induced concentration (50 mg/l)

	First-order model			Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model		
Adsorbent	q_e (cal)	K_1	R^2	q_e (cal)	K_1	R^2	q_e (cal)	K_1	R^2	q_e (cal)	K_1	R^2
Lead (Pb)												
HC	1.2144	0.0291x	0.9909	4.5398	0.0097x	0.9741	0.0046	0.0243x	0.9986	1.8337	0.0797x	0.9831
HG	1.3205	0.0133x	0.7485	4.4667	0.0073x	0.7923	0.0068	0.029x	0.9912	1.773	0.0538x	0.5104
Chromium (Cr)												
HC	1.4899	−0.142x	0.9706	4.29	0.0154x	0.9585	0.0217	0.0343x	0.9883	1.5579	0.01546x	0.8278
HG	1.5619	−0.005x	0.9841	4.1351	0.0115x	0.9785	0.0259	0.054x	0.991	1.4322	0.1126x	0.9394

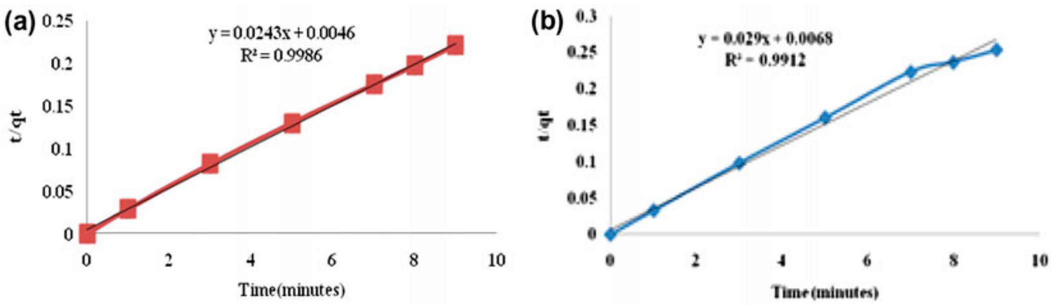

Fig. 7. Plot of pseudo-second-order kinetics for adsorption of lead (Pb) using glucose–alumina hybrid from greener (a = HG) and conventional (b = HC) precursor.

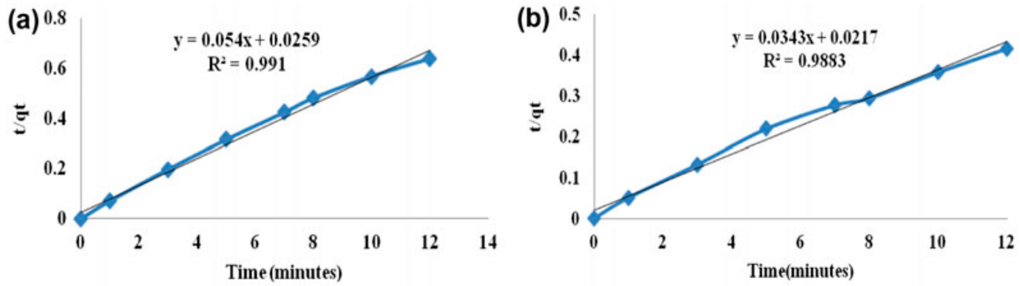

Fig. 8. Plot of pseudo-second-order kinetics for adsorption of chromium (Cr) using glucose–alumina hybrid from greener (a = HG) and conventional (b = HC) precursor.

Table 3
Freundlich isotherm of lead (Pb) and chromium (Cr) using glucose–alumina hybrids from conventional (HC) and greener (HG) precursor at induced concentration (50 mg/l)

	Lead (Pb)						Chromium (Cr)					
	Freundlich isotherm			Langmuir isotherm			Freundlich isotherm			Langmuir isotherm		
Adsorbents	q_e (cal)	K_1	R^2	q_e (cal)	K_1	R^2	q_e (cal)	K_1	R^2	q_e (cal)	K_1	R^2
HC	5.7487	$-2.9643x$	0.991	8.924	0.3233	0.9671	2.664	$-0.912x$	0.9894	0.0741	$-0.8217x$	0.958
HG	2.1655	$0.5281x$	0.994	0.046	$-0.275x$	0.9797	2.09	$-0.465x$	0.9936	0.043	$-0.2134x$	0.974

hydrogen bonding (physisorption) is the prime source of binding.

Adsorption is a time dependant parameter as time is required for adsorbate to diffuse in to the adsorbent [37,38]. The adsorption batch experiments are investigated till the achievement of equilibrium.

3.5. Adsorption kinetics

Kinetic study of the adsorption gives an important insight to understand the mechanism. The present study is an attempt to understand the adsorption rate and sorption capacity. Kinetics is investigated and different kinetic models are applied to explore the best fit model. The results are summarized in Table 2. The results clearly indicate that pseudo-second-order is best fit to explain the adsorption of lead (Pb) and chromium (Cr) (Figs. 7 and 8).

3.6. Adsorption isotherms

To conduct the isotherm studies, two models were used: Freundlich and Langmuir. The results are summarized in Table 3. The isotherm study indicates that the adsorption of Pb and Cr in the HC and HG follow the Freundlich model (Figs. 9 and 10).

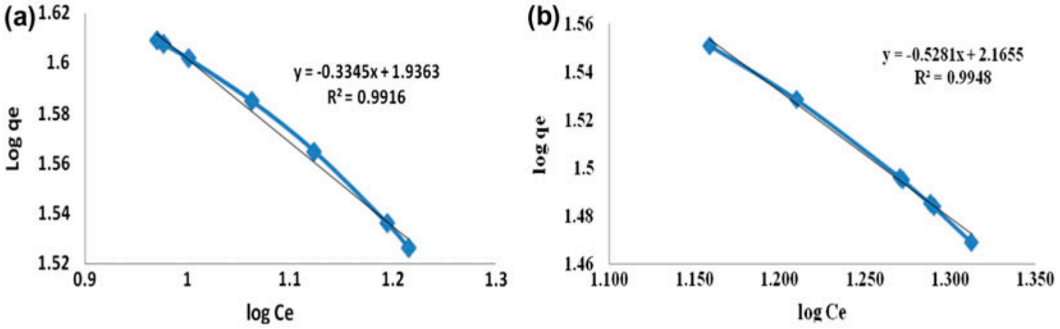

Fig. 9. Freundlich isotherms for the adsorption of lead (Pb) using glucose–alumina hybrid from conventional (a = HC) and greener (b = HG) precursor.

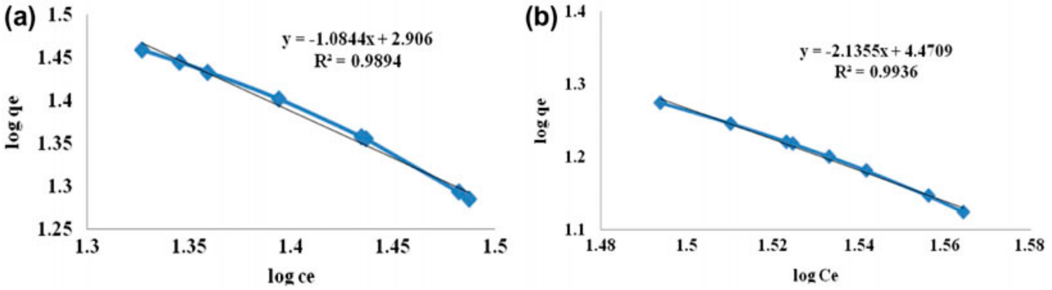

Fig. 10. Freundlich isotherms for the adsorption of chromium (Cr) using glucose–alumina hybrid from conventional (a = HC) and greener (b = HG) precursor.

4. Conclusions

The present study can be concluded as follows:

(1) The method adopted for synthesis of alumina-based hybrids is novel, simple, convenient, and greener using spent foil as a source of aluminum. The successful synthesis from both conventional and greener route is witnessed by different characterization techniques (FTIR, SEM, and EDX).

(2) FTIR spectra indicated the presence of different functional groups (–OH, C–H, Al–O, and Al–O–Al) onto the adsorbent surface, participated in binding for the removal of metals (Pb and Cr). The absorption bands of Al–O–C at 1,386–1,383 cm^{-1} and 1,095–1,093 cm^{-1} region exhibits the synthesis of hybrid.

(3) Alumina-based hybrids are found to be amorphous shaped blocks with small coarse particles. The particle size assessed from SEM micrograph ranges from 26 to 40 nm. Small crevices and holes can also be seen that are expected to participate in adsorption process.

(4) The elemental composition of hybrids indicates significant amount of 29–44%, aluminum, carbon = 11–23%, and oxygen = 20–39% in as synthesized glucose–alumina hybrids from green and conventional precursor.

(5) The synthesized hybrids are proven to be good adsorbents for the removal of metals (Pb and Cr), showed 88% Pb and 58% Cr removal using hybrid (HC) synthesized from conventional precursor while 85% Pb and 38% Cr removal using hybrid (HG) using greener precursor.

(6) Pseudo-second-order and Freundlich isotherms are best fit to experimental data.

Hence, greener synthesis (using spent aluminum foil) results are comparable to conventional one. It is revealed that the spent aluminum foil and glucose as inorganic and organic moiety can be used in place of expensive metal salts and alkoxides. Both exhibiting good efficiency for hybridization is evident from FTIR, SEM, and EDX results. The present work explored environmentally friendly, economical, and cost-effective alternative to costly synthetic adsorbents for the removal of metals (Pb, Cr) from aqueous media. It will also help in the management of solid waste material converting the waste material into value-added products.

5. Recommendation

Following recommendation can be of use in the future

(1) As synthesized glucose–alumina hybrids can be functionalized with different organic functional groups (amine, thiol and many others) to further enhance its adsorption capacity.

(2) It is also recommended that the synthesized hybrid can be used to synthesize the thin film, nano-, and ultrafiltration membranes for water purification.

Acknowledgments

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Conflict of interest

The authors certify that there is no conflict of interest with any financial organization regarding the material discussed in the paper.

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