Advances in water treatment by adsorption technology

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Among various water purification and recycling technologies, adsorption is a fast, inexpensive and universal method. The development of low-cost adsorbents has led to the rapid growth of research interests in this field. The present protocol describes salient features of adsorption and details experimental methodologies for the development and characterization of low-cost adsorbents, water treatment and recycling using adsorption technology including batch processes and column operations. The protocol describes the development of inexpensive adsorbents from waste materials, which takes only 1–2 days, and an adsorption process taking 15–120 min for the removal of pollutants. The applications of batch and column processes are discussed, along with suggestions to make this technology more popular and applicable.

INTRODUCTION

Water is an important and essential component of this universe and plays a vital role in the proper functioning of the Earth's ecosystems. In spite of this, safe drinking water is not available in some parts of the world. The quality of water resources is deteriorating exponentially because of their contamination. Both point and non-point sources are polluting our water resources as a result of tremendous population growth, modern industrialization, civilization, domestic and agricultural activities and other geological, environmental and global changes. Nowadays, water pollution is a serious issue because it affects our lives[1–3] and is expected to get worse over coming decades. More than seven hundred organic and inorganic pollutants have been reported in water along with microbial populations. Among these, certain organic and inorganic pollutants are dangerous because of their highly toxic and carcinogenic nature[4,5]. Moreover, some organics and metal ions are not biodegradable or bio-transformable and, hence, persist in the environment for a long time. Most toxic organic pollutants are pesticides, polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), plasticizers, phenols and drug residues whereas toxic metal ions include arsenic, cadmium, platinum, mercury and antimony among others[6–11]. Therefore, water treatment and recycling of polluted and waste water are the best approaches to get safe water for our routine activities.

Various methods for water purification and recycling have been developed and used[12–23]. The most important are reverse osmosis, ion exchange, electrodialysis, electrolysis and adsorption. Among these, reverse osmosis, ion exchange, electrodialysis and electrolysis are costly technologies with a 10–450 US$ per million liter cost for treated water. The cost of treated water by adsorption varies from 10 to 200 US$ per million liters. Adsorption is a fast, inexpensive and widely applicable technique[23]. Moreover, it is universal in nature as it can be applied for the removal of soluble and insoluble contaminants and biological pollutants with removal efficiency of 90–99%. At an industrial level, pollutants are removed from water by using columns and contractors filled with suitable adsorbents. Adsorption can also be used for source reduction, reclamation for potable, industrial and other purposes. As a result, much work has been carried out on water treatment by adsorption. In this protocol, we include an introduction to adsorption technology, a protocol and applications for water treatment and recycling.

Adsorption

Adsorption is a surface phenomenon and is defined as the increase in concentration of a particular component at the surface or interface between two phases[19]. Compound (pollutant) that sticks or adheres to the solid surface is called an adsorbate and the solid surface is known as an adsorbent. Adsorption is affected by temperature, the nature of the adsorbate and adsorbent, the presence of other pollutants and atmospheric and experimental conditions (pH, concentration of pollutants, contact time and particle size of the adsorbent). The presence of suspended particles, oils and greases reduces the efficiency of the process and, therefore, pre-filtration is sometimes required. When a finely divided solid is shaken with the contaminated and/or polluted water, the pollutants adhere to the solid surface and a stage of equilibrium is established. At this stage, the concentrations of pollutants adsorbed and in the water become constant. The relationship, at a given temperature, between the equilibrium amounts of pollutant adsorbed and in the water is called an adsorption isotherm. Langmuir, Freundlich and other models are well known and can explain the adsorption efficiency of a pollutant systematically and scientifically[19]. Development and optimization of adsorption parameters can be carried out by batch and column processes in the laboratory. The adsorption technology is then applied at pilot and industrial scales by using large columns.

Protocol

This protocol comprises the detailed experimental procedure for water treatment by adsorption technology. It includes reagents, equipment, preparation of adsorbents and their characterization, development of adsorption technology by batch and column processes on a laboratory scale, water treatment economically on a large scale by column operations and applications of this technique. These steps are described in the following sections. An outline of the protocol for water treatment and recycling is given in **Figure 1**.

Development and characterization of adsorbents

Since the introduction of adsorption in the 1940s, activated carbon has been the first choice for the treatment and recycling of municipal and industrial waste water to a potable water quality because of its good adsorption capacity owing to small particle size and active free valancies[13,24]. In spite of this, it cannot be used as an

adsorbent for water treatment on a large scale because of its high cost of production and regeneration. These drawbacks attracted scientists to develop low-cost adsorbents by using a wide range of carbonaceous and other precursors[25,26]. Many starting materials for this purpose are from industrial and agricultural by-products. The use of waste products as adsorbents also contributes towards waste management, recovery and re-use[25,26]. Many alternative feed stocks have been proposed and used for the preparation of activated carbon. In addition, other inorganic precursors have been converted into low-cost adsorbents[22].

Batch experiments

The development of the batch adsorption process starts with plotting the isotherm. A typical plot is shown in **Figure 2**. This is an equilibrium graph plotted between adsorbate concentrations of adsorbed per gram of adsorbent and in aqueous phase, respectively, at equilibrium (C_e). Basically, maximum adsorption of pollutants on a particular adsorbent can be achieved by optimizing various parameters of adsorption. The most important parameters have already been discussed above. Adsorption batch experiments can be carried out as described in the protocol. Study of the kinetics is also a very important step to understand the adsorption mechanism and to design columns on laboratory, pilot and industrial scales. Experimental procedures for determining the kinetics are summarized below.

Column experiments

Once optimized conditions of adsorption are determined by batch experiments, these can be transferred to column operations. The designing of a column starts with laboratory testing to determine the breakthrough capacity. A mass transfer zone is formed in the column bed by passing contaminated water through. The depth of this zone is controlled by the characteristics of the adsorbent, pollutants and hydraulic factors. The depth of the mass transfer zone is a measure of the physical and chemical resistance to mass transfer. This zone moves down and reaches the bottom of the column, where pollutant concentrations in the effluent become equal to the influent concentrations and the breakthrough point of the column occurs. This situation is illustrated in **Figure 3**. The breakthrough curve is idealized by the assumption that the removal of the pollutants is completed over the initial stages of operation. The break point is chosen arbitrarily at some low value, C_b for the effluent concentration. At an arbitrarily selected effluent concentration, C_x closely approaching C_0, the sorbent is considered to be essentially exhausted. Total mass quantity of effluent V_b, passing
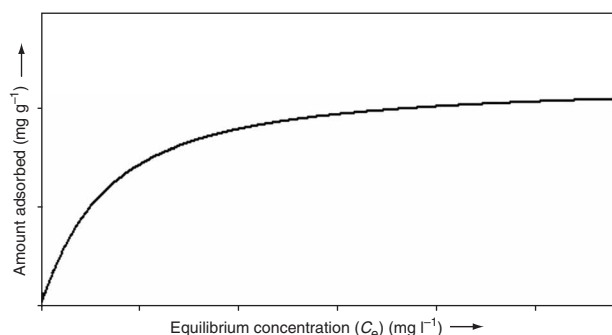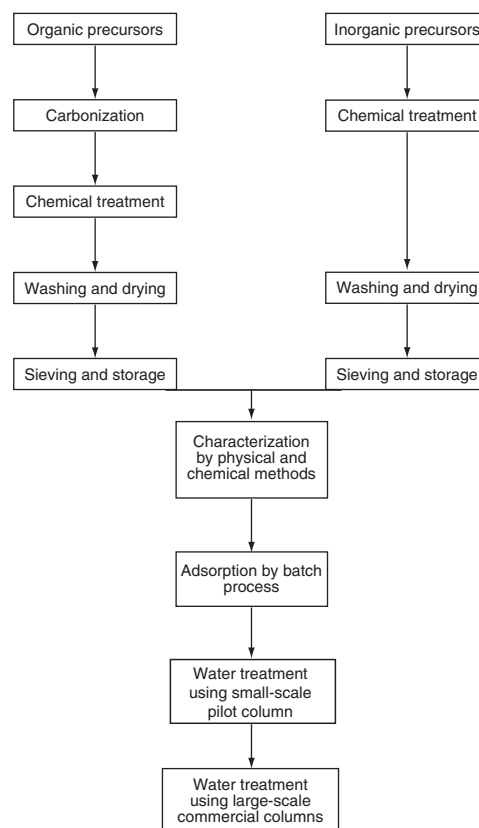

Figure 1 | Protocol for water treatment and recycling by adsorption technology.

per unit cross-section at the break point, and the nature of the breakthrough curve (between the values V_b and V_x) are used for design purposes. The primary adsorption zone in the fixed bed adsorbent is that part of the bed where there is a concentration reduction from C_x to C_b. It is assumed to be of constant length (L_m). Total time tx involved for primary adsorption zone formation may be calculated using

$$tx = V_x/F_m,$$

where F_m is mass rate of flow to the adsorber expressed as mass per unit time per unit cross-sectional area of the bed. The fractional capacity (f) of the adsorbent at break point may be calculated using

$$f = \int_0^1 [1 - C/C_0]d[(V_e - V_b)/V_x - V_b].$$

Percent column saturation at break point is given by

$$\% \text{ Saturation} = [D + L_m(f - 1)]/D,$$

where D is adsorbent bed depth.

Column operation for water treatment is carried out by adopting the following procedure. The time required for each step is important and is indicated where appropriate. The determination of adsorption time interval, i.e., contact time, is important in the batch process and is fixed experimentally at the start. Contact time depends on the type of adsorbent and adsorbate, and varies from 15 min to a few hours in both batch and column operations. However, an adsorption method with the minimum contact time interval is ultimately the best.

Figure 2 | A typical batch adsorption isotherm indicating equilibrium stage at adsorption.

MATERIALS
REAGENTS
· Hydrogen peroxide
· HCl
· NaOH
· Standard solution of pollutant
· Phosphate, acetate and borate buffers of different concentrations and pH
· Solvents for regeneration of exhausted adsorbents (*n*-hexane, cyclohexane, toluene, *m*-xylene, styrene, *1,1,1*-trichloroethane, dichloromethane, tetrachloroethylene, ethylacetate, acetone, methyl-ethylketone, methylisobutylketone, methanol, ethanol, *n*-propanol, *n*-butanol etc.)

EQUIPMENT
· X-ray diffractometer
· Scanning electron microscope (SEM)
· IR spectrometer
· UV–vis spectrometer
· Atomic absorption spectrometer (AAS)
· Gas chromatograph mass spectrometer (GC-MS)
· Liquid chromatograph mass spectrometer (LC-MS)
· Ion chromatograph
· Inductively coupled plasma (ICP)
· Capillary electrophoresis (CE) apparatus
· Quantasorb surface area analyzer
· Vacuum dessicator

REAGENT SETUP
Standards The standard chemicals needed depend on the kind of the pollutants present in the water. These pollutants are required in pure form as standards. The most commonly used standards are pesticides (organochlorine and organophosphorous), polynuclear aromatic hydrocarbons (PAHs), poly-chlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs),

plasticizers, phenols, some drug residues and salts of toxic metal ions, such as arsenic, cadmium, platinum, mercury and antimony. Other commonly used chemicals and reagents may also be required.

Adsorbents Suitable materials are required. Waste materials can be converted into low-cost adsorbents. Selection criteria for precursors can include availability, cost, performance and ease of regeneration or management of the used adsorbents. All precursors require certain purification, activation, chemical treatment, operations etc. The most commonly used organic precursors are scrap tires, bark and other tannin-rich materials, sawdust and other woody material, petroleum wastes, rice hulls, fruit stones, coconut shell, fertilizer wastes, peat moss, chitosan, algae, seaweeds and seafood processing wastes, resins, fly ash and wastes of some other industries (see **Supplementary Table 1** online). Inorganic precursors include metal oxides and hydroxides, clays, red mud, zeolites, blast furnace slag, sediment, soil, ore minerals and other materials. Readers should consult our notes on detailed preparation of the adsorbents[22].

EQUIPMENT SETUP
GC-MS, LC-MS or electrophoresis equipment for detection of organic pollutants The working efficiency of adsorption technology is determined by finding out the concentrations of pollutants in the treated water. Therefore, the requirement for equipment depends on the type of pollutants present in the water. Normally, GC-MS, LC-MS and electrophoresis instruments are used to monitor organic pollutants. Analyses of chiral pollutants are carried out by using chiral stationary phases with the above-mentioned instruments.

AAS and ICP instruments for detection of metal ions Metal ions can be determined by using AAS and ICP instruments. For speciation of metal ions, an ion chromatograph is required.

Columns Laboratory, pilot and industrial scale columns are used for adsorption technology.

PROCEDURE
Conversion of waste materials into inexpensive adsorbents
1| Collect selected waste material and sieve to remove other particles such as stone, soil, paper etc.

2| Wash with ddH$_2$O and dry in an oven at 100 °C for about 2 h.

3| Carbonize organic precursors by heating to 400–800 °C for 5–24 h.

4| Treat with hydrogen peroxide at 60 °C for 24 h to remove adhered organic matter.

5| Wash with ddH$_2$O three times to remove hydrogen peroxide and dry in an oven at 100 °C for ∼2 h.

6| Heat to 500 °C in a furnace for 6–12 h to activate the adsorbent.

7| Determine density, porosity and ignition loss by the usual methods[27,28].

8| Establish the stability of the adsorbent by suspending in ddH$_2$O, HCl and NaOH (0.1 to 1.0 M) for about 1–2 h.

9| Establish mineral and crystal structure by X-ray diffractometry and SEM, using published methods[29–32].

10| Carry out elemental analysis by chemical methods, as described[33].

11| Collect adsorbent of different particle sizes by sieving and keep in a vacuum desiccator. At this stage, the adsorbent is ready for water purification.

Batch experiments
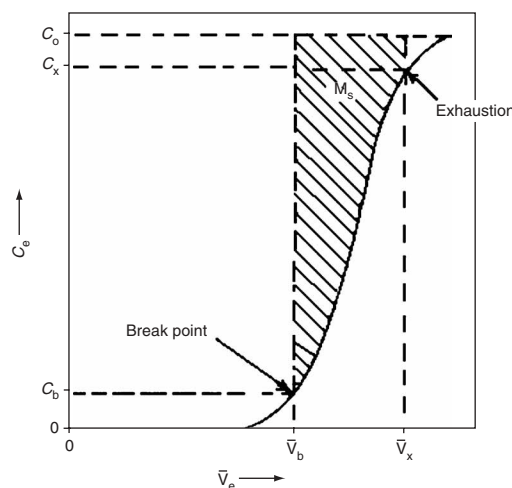**12|** Use a 50-ml Erlenmeyer flask to carry out batch experiments in a thermostatic shaking water bath. Take a

Figure 3 | A typical column breakthrough curve. (C_o = initial concentration of influent, C_x = concentration of effluent at exhaustion, C_b = concentration of effluent at breakpoint, C_e = equilibrium concentration effluent, $\bar{V}_b$ = volume of effluent at breakpoint, $\bar{V}_x$ = volume of effluent at exhaustion, $\bar{V}_e$ = volume of total effluent).

known amount of pollutant in 10–25 ml H$_2$O and add a dose of adsorbent. The dose of adsorbent depends on the type of adsorbent and adsorbate. However, a suggested starting point is 0.5 g l^{-1}. Alter the pH of the solution using HCl or NaOH.

13| Agitate flask mechanically in a water bath at desired temperature. Normally temperature is fixed between 25 and 35 °C for 1–3 h.

14| Repeat Steps 12–13 to optimize concentration of pollutant, pH, adsorbent dose, temperature and contact time after varying their values.

15| Centrifuge or filter the mixture and determine the concentration of pollutant in the aqueous phase.

16| Calculate the amount of pollutant adsorbed from the aqueous solution by determining the equilibrium concentration in solution.

Kinetic studies

17| Set up 50-ml Erlenmeyer flasks containing various amounts of standard solutions of pollutant and shake in a thermostatic shaking water bath.

18| Add a known amount of adsorbent to each flask.

19| Allow flasks to agitate mechanically in the water bath at a constant temperature. Contact time, temperature and other conditions should be selected based on preliminary experiments.

20| Centrifuge the mixture at pre-decided time intervals and analyze the concentration of pollutant in the supernatant. Adsorbent particle size is an important variable in deciding centrifugation timings. Normally, this varies from 30 to 60 min at 5,000–100,000g.

21| Determine the equilibrium concentration (C_e) and time to reach equilibrium.

22| Calculate thermodynamic parameters as detailed in the INTRODUCTION and run adsorption models.

Column experiments

23| Design a column of pyrex glass on a laboratory scale of about 50 × 2 cm size. Attach a manometer on the right-hand side by using two pressure points to monitor the introduction of air into the column, if any (**Fig. 4**).

24| Fix 250-B.S.S. (British standard size) mesh wire gauges at the pressure points to prevent entry of the adsorbent particles into these points.

25| Cover the upper end of the column with a tube connection to remove any air bubbles.

26| Attach the upper end to a head tank from which the flow of contaminated water is regulated.

27| Control the flow of contaminated water by a stopper point at the lower end of the column.

28| Fix supporting medium (glass wool) at the lower end of the column by hydraulic filling.

29| Weigh out adsorbent material and make a slurry in ddH$_2$O. Use slurry within 24 h.

30| Fill the column and stir using a glass rod, then leave undisturbed overnight to settle.

31| Load contaminated water on top of the column and adjust the flow rate to achieve maximum uptake of pollutants and use the column up to its saturation point.
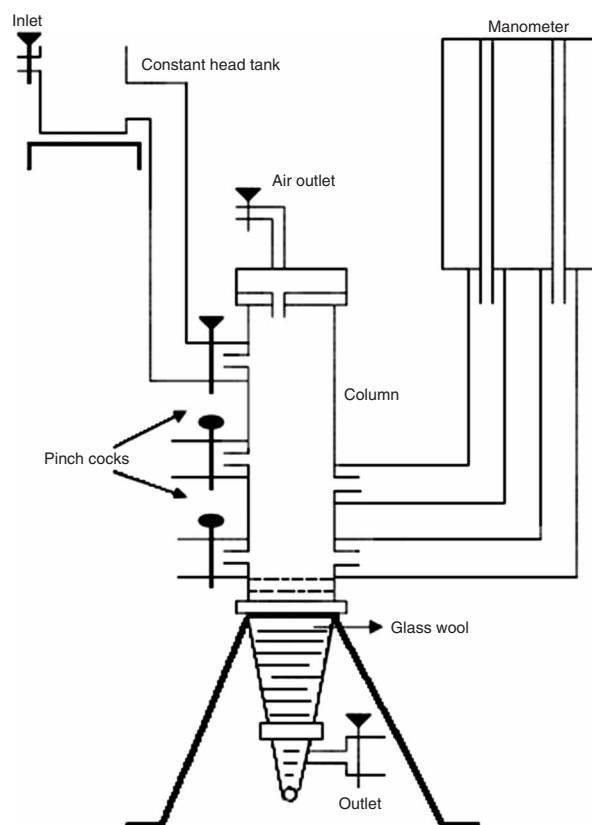

Figure 4 | Schematic diagram of a column used for water treatment by adsorption technology.

32| Regenerate the column for recycling of adsorbents by using acid or base or buffers or organic solvents depending on the type of pollutants adsorbed on the adsorbent or decide on the management methods for used adsorbent.

33| Calculate the amount of pollutant adsorbed on the adsorbent and determine the capacity of the column by drawing a breakthrough capacity curve.

34| Design and fabricate pilot and industrial scale columns for treatment of contaminated water at larger scale.

● **TIMING**
Preparation of adsorbents (Steps 1–11): 4–5 d
Batch experiments (Steps 12–16): 1–2 d
Kinetic studies (Steps 17–22): 1–2 d
Column experiments (Steps 23–34): 1–2 d

? TROUBLESHOOTING
There are no significant problems in the adsorption technology methods. However, certain problems may be faced in the use of instruments for the detection of pollutants. Troubleshooting advice can be obtained by consulting the manuals of the instruments concerned. Chromatographic and capillary electrophoretic instruments are quite sensitive and, hence, need experienced and versatile hands to determine the exact concentration values of the pollutants.

ANTICIPATED RESULTS
The majority of publications available on adsorption deal with the development of adsorption technology by optimizing experimental variables in batch process mode only. Kinetics data are interpreted and discussed by calculating values of enthalpy (ΔH), free energy (ΔG), energy of activation (E_a) and entropy (ΔS) by using well known kinetics equations. Some workers treat kinetics data by using the Boyed model to understand the practical application of the process. Various models such as Langmuir, Freundlich, Temkin, Triple-Layer, Redlich-Peterson, Brunauer-Emmett-Teller (BET), McKay, etc. are used to test the validity of the adsorption process. Removal of some common pollutants by batch processes is summarized in **Supplementary Table 1**.

Basically, the batch process provides basic and initial knowledge of adsorption, which is useful to design and fabricate columns. The transfer of batch experimental conditions to columns requires special attention and skill. Normally, the bed-depth-service-time (BDST) model, proposed by Hutchins[34] is used to validate the results obtained from column operations. Despite a great need for column operations in water purification, little work has been carried out in this direction. The design and other operational column conditions have already been discussed above. However, the column design shown in **Figure 4** was found suitable for the removal of many organic and inorganic pollutants from water by using low cost adsorbents in our laboratory.

Numerous substances have been successfully used as absorbents in column experiments. The absorbent capacities of leaves of 34 conifer species have been evaluated[35] with, for example, 27.5 mg g^{-1} as maximum adsorption capacity of *Gingko biloba* leaves for Cr(III). Column capacities for Cr(VI) uptake were 8.9 mg g^{-1} and 6.3 mg g^{-1} for commercial carbon and rice husk carbon (RHC), respectively[36]. These adsorbents were successfully used for the treatment of actual waste water from a plating shop bearing Cr(VI) up to 300 mg l^{-1}. Crude shrimp chitin was packed in small columns and used for the removal of Cu(II), Cr(III) and Ni(II) metal ions from solution[37]; about 92–96% Cu(II) was removed from the effluent from electroplating industry. Leusch *et al.*[38] used brown marine algae, *Ascophyllum nodosum*, for the removal of Cd(II) with a maximum adsorption capacity of 67 mg g^{-1}. Blast furnace slag was used in a column for the removal of zinc, cadmium, copper and nickel from the effluent of a metal finishing plant[39]. Similarly, Gupta *et. al.*[40] also used this adsorbent for the removal of lead and chromium from waste water. In another study, the same group[41] reported removal of lead from aqueous solution by using column experiments. Low concentrations of lead were removed at 100% efficiency and higher concentrations at 50–70% efficiency. Experiments with actual waste water from a metal finishing plant bearing 17.0 mg l^{-1} lead provided successful results. It was found that almost complete removal of Pb(II), from 50 ml of waste water at pH 3.2, was possible with 4.0 g l^{-1} adsorbent. Furthermore, Gupta and co-workers have removed chromium[42], copper and zinc[43] from aqueous solutions using a sugar industry waste—bagasse fly ash—in columns. The same adsorbent was used for the removal of DDD and DDE (with 97–98% efficiency)[44] and lindane and malathion (98%)[45]. The removal of phenols and its derivatives was also achieved using red mud at a flow rate of 0.5 ml min^{-1} (ref. 46).

Su and Puls[47] used a column 10.3 cm long filled with iron and sand (50:50, w/w) to reduce arsenite and arsenate contents. A hybrid ion exchanger (HIX) has also been used as the column adsorbent for the removal of arsenic species from ground water[48]. The repeated use of HIXs in various laboratories suggests good attrition-resistant properties, and the columns retain their arsenic removal capacity over many cycles. Polystyrene matrix loaded with manganese dioxide has been used for the removal of As(V) and As(III) species from artificial water, composed of arsenic of granitic water[49]. A good efficiency of

adsorption for the removal of total arsenic is also reported using portland cement as an adsorbent[50]. Takanashi et al.[51] developed a novel adsorbent (activated alumina based) for arsenic removal from the ground water with 10.0 mg g^{-1} adsorption capacity at pH 7.0. The authors compared its capacity with conventional activated alumina, which was 5% higher.

The demand and interest of adsorption technology by column operations has been increasing in recent years and, hence, work in this direction is progressing worldwide. A breakthrough curve was obtained for the removal of lead at 5% breakthrough yielding a BDST sorption capacity of 24.27–35.73 mg g^{-1} (ref. 52). A cellulose column under dynamic conditions for the removal of chlor-alkali from waste water has an adsorption capacity of 65 μg g^{-1} (ref. 53). Bottom ash and de-oiled soya have been used for the removal of indigo carmine dye by column operations with adsorption capacities of 0.0969 and 0.2987 g g^{-1}, respectively[54]. A value of 250 μg g^{-1} is reported for the removal of aluminum from water using a chitosan column[55].

CONCLUSION

As discussed above, adsorption is an effective, efficient and universal method of water treatment providing risk-free treated water as per the guidelines of WHO and EPA. This technology has been used for water treatment by developing low-cost alternatives to activated carbon. By comparison and computation of the adsorbents, based on the performance, adsorption capabilities and cost, it was found that the most important and feasible adsorbents are red mud, sand and fly-ash, because they are freely available, have good adsorption capacities and require little treatment. Moreover, the management of these exhausted adsorbents is not a problem as they can be used in building construction. Owing to the presence of many pollutants in our water resources, widely applicable adsorbents need to be developed that can adsorb organic and inorganic pollutants. As noted above, most researchers deal with the batch process only and, hence, there is a great need to design and develop columns for water purification and recycling purposes on a large scale.

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