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Current Progress of Capacitive Deionization for Removal of Pollutant Ions

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Abstract: A mini review of a recently developing water purification technology capacitive deionization (CDI) applied for removal of pollutant ions is provided. The current progress of CDI for removal of different pollutant ions such as arsenic, fluoride, boron, phosphate, lithium, copper, cadmium, ferric, and nitrate ions is presented. This paper aims at motivating new research opportunities in capacitive deionization technology for removal of pollutant ions from polluted water.

Keywords: Capacitive deionization; membrane capacitive deionization; pollutant ions

1 Introduction

Global availability of fresh water has decreased due to population growth, global warming and huge increases in pollution, such as a widespread release of various organic and inorganic pollutants into the environment [1]. In such conditions developing or applying new technologies for delivering pure water to society has been a growing challenge. Nowadays, worldwide demand of fresh water has rapidly increased. Based on current developments in research activity various techniques are available for treatment of polluted water such as sedimentation, membrane separation, adsorption, coagulation–flocculation, precipitation, chemical reaction, flotation, ion exchange processes and biological processes with varying levels of success [2]. Globally, during the last few years, researchers are much attracted to the newly developing technique capacitive deionization. Generally capacitive deionization technology was used for desalination. CDI has better performance in removal of divalent ions [3] and in purification of insulin [4]. Microbial fuel cells act as a power source in CDI for feeds of low salinity [5, 6]. Recently, researchers are much more interested in CDI technique for removal of toxic ions. In this minireview, we present a general overview about removal of pollutant ions by capacitive deionization.

2 Capacitive deionization and membrane capacitive deionization (MCDI)

CDI works on the principle of electrostatic adsorption using porous electrodes. In a CDI transport of ion is due to electrostatic adsorption, not due to oxidation and reduction reactions [7]. CDI has benefits of being eco-friendly, having less energy consumption and working costs than other desalination technologies, simplicity in regeneration and maintenance compared with other conventional techniques of desalination [8, 9]. In capacitive deionization techniques one or several pairs of oppositely charge electrodes are used as a capacitor for deionization of water. Electrodes used in CDI have a positive and negative pole under the application of external voltage. The salt solution contains positively and negatively charged ions, namely cations and anions, respectively. These ions are captured by oppositely charged electrodes due to electrostatic force under application of electric potential. Purification and regeneration are the two important operating steps used in CDI technology. In purification mode ions are captured or deposited on oppositely charged electrode under application of potential difference and pure water stream comes out from the CDI cell. When the electrodes getting saturated due to sorption of ions there is a necessity of desorption of ions from that electrode. In such conditions either reversed potential difference is applied or zero voltage is applied to the electrodes for removal of ions from electrodes and the outlet of CDI cell contains a highly concentrated solution. Schematics of purification mode and

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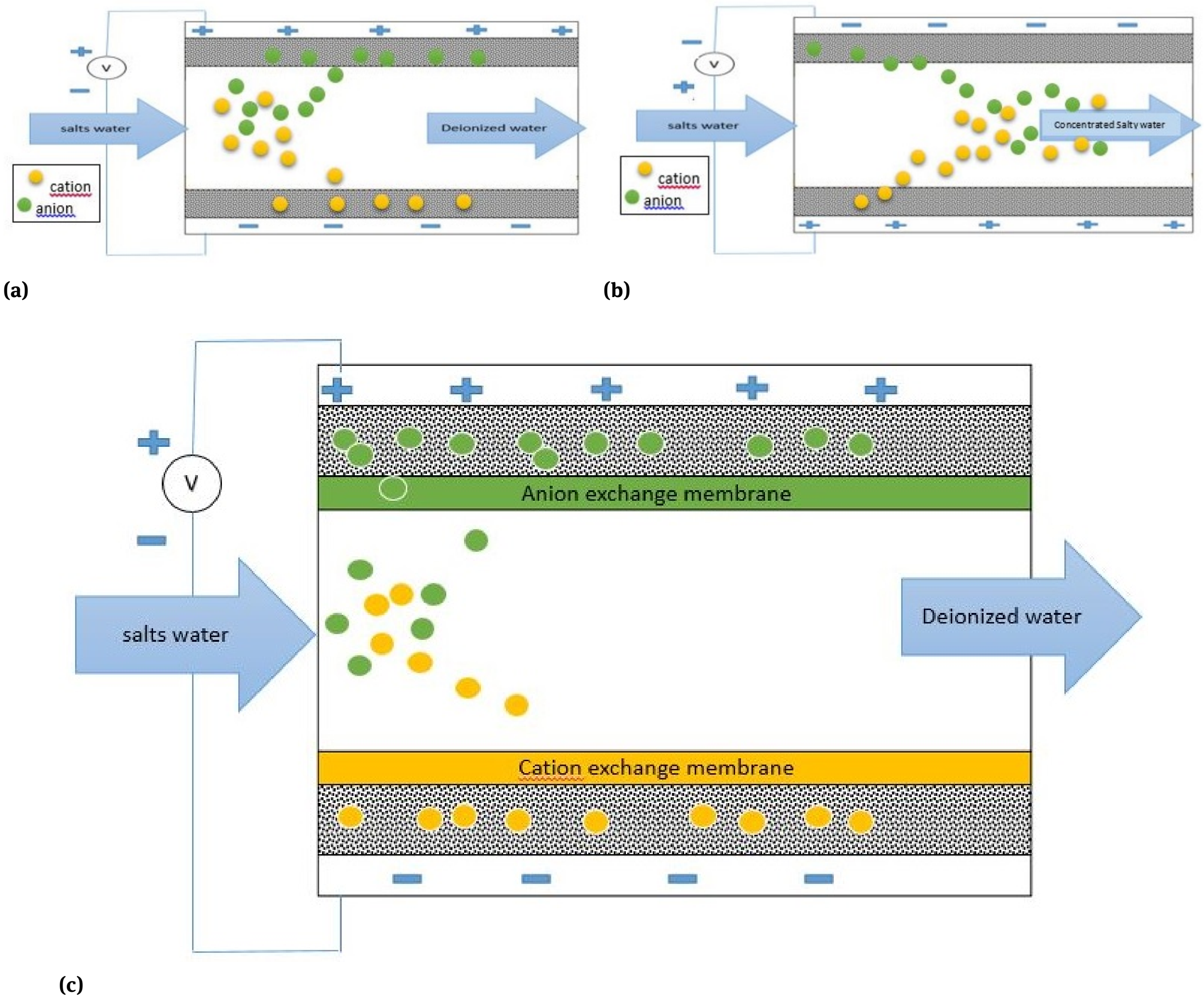

Figure 1: (a) CDI purification mode, (b) CDI regeneration mode, (c) membrane capacitive deionization.

regeneration mode are presented in Fig. 1. Recently, ion exchange membranes are used in CDI systems that are called membrane capacitive deionization (MCDI) systems. Working mechanism is shown in Fig. 1(c). In MCDI ion exchange membranes are placed in front of porous electrode operated by applying a potential difference [10, 11]. Cation and anion exchange membranes are placed in front of negative and positively charged electrodes, respectively, and are separated by inserting a non-conductive spacer in between them to avoid short circuit. Ion exchange membrane role is to keep away counter ions. Finally, pure water come out at the outlet of MCDI cell. In MCDI co-ion effect, *i.e.* coadsorption of ions with opposite charge because of *e.g.* specific interactions between ions, is restricted.

3 Electrode materials in CDI

Removal efficiency has been enhanced by application of novel electrodes synthesized from single materials and composites [12]. Electrodes used in CDI have a high surface area and wettability, better electrical conductivity, and suitable pore arrangement for removal of ions in sea water have been reported [13, 14]. Worldwide carbon materials are attractive for preparation of electrodes due their properties [15]. Normally activated carbon [16], mesoporous carbon [15] and carbon aerogels [17, 36] are used as carbon materials for electrode preparation. Recently application of nanomaterial-based electrode has yielded better response in desalination [18, 19]. Mostly graphene as high performance electrode material is suggested for capacitive deionization [20]. Merging metal oxides with nanostructured graphene improves capacitance [21–23]. Also nanostructured electrodes [24] and polymer-coated electrodes [25] were used for capacitive deionization.

4 Current status of CDI in pollutant ion removal

The current state of CDI for removal of pollutant ions (arsenic, fluoride, boron, phosphate, lithium, copper, cadmium, ferric ion, and nitrate) is comparatively and systematically collected in Table 1.

5 Discussion of pollutant ion removal by CDI

A graphene nano-flake (GNFs) electrode was fabricated for capacitive deionization because of better specific surface area and good electronic conductivity and such electrode was employed for ferric chloride electrosorption. An electrosorption capacity of 0.5 mg/g for an initial concentration of $FeCl_3$ was reported. Electrosorption experiments were carried out for different ions and GNFs electrode results were found in the order $Fe^{3+} > Ca^{2+} > Mg^{2+} > Na^{+}$ [26]. Removal of boron present as boric acid form in water by CDI with activated carbon electrodes was reported by Avraham *et al.* [27]. It was removed in two steps. In the first step dissociation of boric acid proceeded done on the negative electrode due to local basic pH caused by polarizing the cell. Then electrosorption of borate ions was done at the positive electrode [27]. Zhang and coworkers reported that solar-powered capacitive deionization could be used for removal of arsenic from water. A Box–Behnken statistical experiment design was used to examine the effects of major process parameters. Experimental values and predicted values of arsenic removal were found good agreement. Removal of arsenate ions by CDI favors lower salinity conditions and high pH [28]. Electrosorption of Cu^{2+} ions from aqueous solution by activated carbon electrodes was reported by Huang and coworkers [29]. At comparatively low voltage, electrodeposition of copper is restricted and Cu^{2+} ions removal on surface of electrode is due purely to electrostactic interaction in the electrical double-layer created in the nanoporous area. Further electrosorption experiments confirmed that Cu^{2+} ions are removed very selectively in a competitive environment over NaCl and NOM [29]. A study of a commercial CDI unit used for treatment of phosphate wastewater with various operating parameters was reported by Huang *et al.* [30]. Maximum removal (at flow rate 4.8 L/min and 50 mg P/L initial concentration) of phosphate was found to be 86.5%. The reported energy consumption was 7.01 kWh/kg P (removed) (or 1.65 kWh/m^3) [30]. Ryu *et al.* suggested a novel system for recovery of lithium with the help of electrostatic field assistance (EFA) to improve the conventional adsorption process. They prepared a lithium-selective electrode with a lithium selective adsorbent and the hydrophilic PVA binder. A test set was fabricated by modifying the conventional MCDI technique. The adsorption performance for lithium by EFA was superior to that found with plain physisorption in the range of the initially tested lithium concentrations. The suggested system also showed good reproducibility and durability during repeated adsorption/desorption cycles [31]. A study of removal of Cd(II) ions from aqueous solution with a newly prepared manganese oxide/active carbon fiber (MO/ACF) electrode was reported by Chen *et al.* [32]. Results prove that the electrosorptive capacity of MO/ACF electrode was six times greater as compared to ACF. It has a greater adsorptive capacity compared to pure ACF because of more adsorptive sites and higher capacitance of MO/ACF [32]. Hu *et al.* reported preparation of a manganese dioxide/carbon fiber (MnO_2/CF) electrode by anodic eletrodeposition and applied it for electrosoption of Cu^{2+} ions [33]. Uniform distribution of MnO_2 nanoflowers with several “petals” was observed on the surface of the carbon fibers. MnO_2/CF electrode showed maximum adsorption capacity (172.88 mg/g) which was two times that of simple MnO_2 absorbent without an electric field imposed [33]. Work on removal of fluoride and nitrate removal by batch-mode CDI from brackish groundwaters was examined by Tang *et al.* [34]. Removal experiments were carried out under different conditions such as feed concentration, flow rate and copresence of sodium chloride. At constant concentration of sodium chloride, fluoride concentration was found to decline in the effluent with declining initial fluoride concentration. At higher initial concentration of chloride a higher equilibrium dissolved concentration of fluoride was found because of competitive electrosorption between fluoride and chloride for the limited pore surface sites. The authors established a one-dimensional transport model for dual anions and found, that it consistently explains the dynamic process of removal of both fluoride and chloride ions in CDI cells at well-defined operating conditions. It was used also successfully for explanation of nitrate removal from brackish groundwaters [34].

As(III) and As(V) removal by CDI with activated carbon electrodes was reported by Fan and coworkers [35].

Table 1: Current status of CDI in removal of pollutant ions.

Pollutant ion	Electrode Material	Electrode dimension W×L×T [mm^3]	Surface area [m^2/g]	Cell type	Initial ion concentration [mg/L]	Voltage [V]	Flowrate [ml/min]	Removal effi-ciency [%]	Electro-sorption capacity [mg/g]	Publication Year and Refer-ences
Arsenic	Activated carbon	158×174×0.3	800	CDI Unit	0.04 0.1	1.5	3000	82.6 98.15	–	2016 [28]
As(V)	Activated carbon				0.1 0.2 50 100 200	1.2	5		1.16×10^{-2} 2.47×10^{-2} 5.52 7.08 10.31	2016 [35]
As(III)	Activated carbon	–	–	–	0.1 0.2 50 100 200	1.2	5		0.77×10^{-2} 1.37×10^{-2} 2.85 5.03 7.57	2016 [35]
Boron	Activated carbon cloth	−×−×0.26	1440	CDI	480	1.0	15	30	–	2011 [27]
Cadmium(II)	Manganese oxide/active carbon fiber	10×20×4	–	CDI	50	1.5	–	80.77	14.88	2015 [32]
Copper(II)	Activated carbon sheet	80 × 80 × –	964	CDI	50	0.8	10	–	24.57	2014 [29]
Copper(II)	Manganese dioxide/ Carbon fiber	30×20×–	–	CDI	6	0.8	–	90	172.88	2015 [33]
Fluoride	Activated carbon	−×−×−	–	CDI system	20	1.6	4600	~ 66.5	–	2015 [34]
Ferric ions	Graphene nano-flakes	70×140×0.3	2600	CDI	20	2.0	25	–	0.88	2010 [26]
Lithium	Carbon electrodes	100×100×0.2	1260	MCDI	5 50 500	2.0 1.0 1.0	20	–	~ 0.5 ~ 1.9 ~ 3.7	2015 [31]

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Nitrate	Activated carbon	–×–×–	–	CDI system	300	1.6	4600	–	–	2015 [34]
Phosphate	Activated carbon	100×100×–	–	CDI pilot plant	50 300	1.5	4800	86.5 77.4	–	2014 [30]

Concluded

Result found that sorption capacity is superior in the case of As(V) compared to As(III) because of the greater negative charge of the prevalent As(V) species. Results prove that electrosorption could be responsible for removal of As(V) whereas in case of As(III) the oxidation of As(III) to As(V) is involved which could then be electrostatically adsorbed on the anode surface [35].

6 Conclusions

The capacitive deionization technology could be a promising technology in the field of pollutant ion removal due to its low energy consumption and ecofriendly regeneration of electrodes. According to literature reported successive removal of pollutant ferric ions, boron, arsenic(III) and (V), copper(II), phosphate, lithium, cadmium (II), fluoride, nitrate, have been realized. Great progress in capacitive deionization technology for ground water and wastewater treatment is expected.

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