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भारत सरकार GOVERNMENT OF INDIA पेटेंट कार्यालय THE PATENT OFFICE पेटेंट प्रमाणपत्र PATENT CERTIFICATE (Rule 74 Of The Patents Rules)

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प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित AN INTEGRATED CDI ELECTRODE नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 30th day of December 2017 से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled AN INTEGRATED CDI ELECTRODE as disclosed in the above mentioned application for the term of 20 years from the 30th day of December 2017 in accordance with the provisions of the Patents Act, 1970.



अनुदान की तारीख : 27/08/2020 Date of Grant : पेटेंट नियंत्रक Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, **30th day of December 2019** को और उसके पश्चात प्रत्येक वर्ष मे उसी दिन देय होगी। Note. - The fees for renewal of this patent, if it is to be maintained will fall / has fallen due on 30th day of December 2019 and on the same day in every year thereafter.

FORM 2

THE PATENTS ACT, 1970

(39 OF 1970)

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The Patents Rules, 2003 COMPLETE SPECIFICATION

(Refer section 10 and rule 13)

TITLE OF THE INVENTION:

AN INTEGRATED CDI ELECTRODE

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3. Preamble to the Description

COMPLETE SPECIFICATION

The following specification particularly describes the invention and the manner in which is to be performed.

COMPLETE SPECIFICATION

FIELD OF THE INVENTION

The present invention relates to the use of capacitive deionization (CDI) technology for the removal of salts from brackish water.

BACKGROUND OF THE INVENTION

The availability of clean potable water at an affordable cost is a growing challenge for mankind. Drinking water is in jeopardy due to growing population, climatic changes and
contamination of various water resources [Hoekstra, A. Y.*et al.*, Nature Clim. Change, 2014, 4, 318-320; Pugazhenthiran, N.*et al.*, ACS Appl. Mater. Interfaces, 2015, 7, 20156-20163; Schewe, J.*et al.*, PNAS, 2014, 111, 3245-3250; Shannon, M. A.*et al.*, Nature, 2008, 452, 301-310]. To meet the growing demand of drinking water, many materials and methods (i.e. reverse osmosis (RO), ultrafiltration (UF), adsorption, photocatalytic degradation and distillation, etc.) are being

- 15 used. Some of these techniques are expensive and they consume high energy [Porada, S.*et al.*, ACS Appl. Mater. Interfaces, 2012, 4, 1194-1199].Capacitive deionization (CDI) is a growing technology which involves adsorption and desorption processes making it both energy and cost efficient than many of the aforementioned methods of desalination of brackish water. When a potential difference is applied to a pair of porous carbon electrodes, cations and anions move
- 20 toward cathode and anode, respectively and get adsorbed, thereby generating 'drinkable' water from brackish water. Subsequently, adsorbed ions can be removed from the electrode by reversing the polarity of the electrode which leads to the regeneration of the electrodes and the same surface can be used again for further removal of ions [Porada, S.*et al.*, ACS Appl. Mater. Interfaces, 2012, 4, 1194-1199; Porada, S.*et al.*, Prog. Mater. Sci., 2013, 58, 1388-1442; Suss,
- M. E.*et al.*, Energy Environ. Sci., 2012, 5, 9511-9519; Suss, M. E.*et al.*, Environ. Sci. Technol., 2014, 48, 2008-2015]. CDI is cost-effective having point-of-use utility along with high theoretical efficiency. However, its practical applications for desalination are yet to be recognized and research is being carried out to discover new materials with improved absorption capacities [Porada, S.*et al.*, Prog. Mater. Sci., 2013, 58, 1388-1442; Suss, M. E.*et al.*, Energy

Environ. Sci., 2012, 5, 9511-9519; Suss, M. E.*et al.*, Environ. Sci. Technol., 2014, 48, 2008-2015; Tsouris, C.*et al.*, Environ. Sci. Technol., 2011, 45, 10243-10249; Długołęcki, P. et al., Environ. Sci. Technol., 2013, 47, 4904-4910].

- Various carbonaceous materials and their composites are used as CDI electrodes for
 higher efficiency in terms of salt adsorption capacity in the range of mg/g. Materials such as graphene[Amiri, A. *et al.*, Sci. Rep., 2015, 5, 17503],graphene-like nanoflakes[Wang, H.*et al.*, J. Mater. Chem., 2012, 22, 23745–23748], functionalized reduced graphene oxide(RGO)[Li, H.*et al.*, J. Mater. Chem., 2009, 19, 6773-6779],graphene-carbon nanotubes (CNT) composites [Li, H.*et al.*, Environ. Sci. Technol., 2010, 44, 8692-8697],3D macroporous graphene architectures
- [Wang, H.*et al.*, J. Mater. Chem. A., 2013, 1, 11778-11789],sponge-templated graphene [Jia, B.*et al.*, Chem. Phys. Lett., 2012; 548:23-28],graphene-Fe₃O₄ [Yang, Z.Y.*et al.*, Adv. Funct. Mater., 2014, 24, 3917–3925],graphene chitosan-Mn₃O₄[Xu, X.*et al.*, Sci. Rep., 2015, 5, 8458],RGO-activated carbon (AC) composites and functionalized graphene nanocomposite have shown adsorption capacities of 1.85, 1.35, 3.2, 1.4, 3.9, 4.95, 10.30, 12.7, 2.94 and 3.47 mg/g,
- 15 respectively. One of the targets of the present inventionis to make this technology more energy efficient and cost-effective, both for deionization of seawater and brackish water. Large brackish water resources, especially in the coastal areas, can be used for human consumption and other needs such as those of washing, agriculture and industry by such process. From a materials science point of view, synthesizing new materials and design strategies for novel and improved
- 20 electrodes is a challenging task. Selecting the right material for the electrode, which is energy efficient, is still a vital aspect of the technology. Naturally, the choice of electrode material largely depends on the required performance (desalting capacity and initial salt concentration), system requirements (flow rate and stack configuration) and cost considerations (efficiency, per unit cost and lifetime). However, many researchers are examining methods to improve the
- efficiency of the CDI materials and to reduce the cost. Mostly, carbon materials are used for CDI technology, but for better performance of the CDI, novel materials can be integrated with carbon materials for electrode preparation[Yang, J.*et al.*, Desalination, 2011, 276, 199-206; Zou, L.*et al.*, Water Res., 2008, 42, 2340-2348; Porada, S.*et al.*, Prog. Mater. Sci., 2013, 58, 1388-1442]. Electrode adsorption capacity is not only related to the total pore volume, pore size, pore
 connectivity and surface area of the material but also related to electrical conductivity and electrochemical stability of the electrode. The most important requirements for CDI electrode

materials and their relation to CDI performance are based on: i) large ion-accessible specific surface area, ii) high (electro) chemical stability over the used pH and voltage range (no oxidation) which is important to ensure longevity and system stability, iii) fast ion mobility within the pore network, iv) high electrical conductivity, v) good wetting behavior, vi) low cost,

- vii) scalability and viii) high bio-inertness (prevent the biofouling of the electrode for long-term operation in surface or brackish water). All of these have to be accomplished at a reduced cost. Performing CDI experiment by incorporating ion-exchange membranes (IEMs) in front of the carbon electrodes is called membrane capacitive deionization (MCDI). Covalently bound linkers, sulfonate or quaternary aminecontaining IEMs are mostly used due to their high internal charge
- 10 which plays an important role in selective ion (the counterion) transport. Biofouling would be reduced by using IEMs on top of the carbon electrodes. When a cell voltage is applied to the CDI electrodes, ions with opposite charges known as counterions are adsorbed in the electrical double layers (EDLs) that are formed within the intraparticulate nanostructure within the porous carbon electrodes accessible to the water, while the ions of same charge known asco-ions are removed
- 15 from the electrodes which populate in the spacer channel. These co-ions present in the spacer channel further prevent the counterions to come to the EDLs for further removal and hence, decreases the adsorption capacity. In case of MCDI, due to the presence of the membrane in front of the electrodes, the co-ions are blocked by it which stays in the macropores of the porous carbon region. Counterions from the ion exchange membrane moves to neutralize the charge of
- 20 the co-ions. In the case of MCDI the counterions are adsorbed in the EDLs as well as in the porous carbon electrodes, therefore increase the adsorption capacity of the electrodes. An MCDI system shows higher desalination performance, salt removal rate andlow electrical energy consumption compared to the CDI system. Though MCDI has several advantages than conventional CDI but its major drawback is the weak adhesion between the electrode material and the membranes, which leads to high contact resistance. Another disadvantage is that all the ion exchange membranes are hydrophobic in nature and have poor wetting characteristics. This leads to low removal efficiency of the ions, generally at low salt concentrations.

Electrode materials need to be embedded/printed on a stable conducting surface which often requires the use of a binder that reduces the available surface area, which can be resolved by integrating electro-adsorbent materials with ion-exchange resin via a covalent linkage. The discovery of graphene has made it extremely beneficial for CDI technology. Due to its large

surface area and tunable functionality, it is possible to retain adsorption capacity even while maintaining proper covalent linkages. Selective edge functionalization of reduced graphene oxide (RGO) is possible to create a single molecular construct having both electro-adsorption and ion permeable characteristics. A device using this material for selective anion and cation permeation has been assembled for an efficient covalently linked IERs-CDI electrode. This methodology helps to pre-concentrate the target ions and block the co-ions, which allows rapid brackish water desalination, where the material retains its conductivity and wetting characteristic unlike in the case of MCDI.It is important to point out hear mixing graphene and ion exchange resin without covalent linkage will not produce desired result.

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SUMMARY OF THE INVENTION

The present invention relates to the use of capacitive deionization (CDI) technologyfor removing salts from brackish water and more particularly to the detailed synthesis protocol, fabrication steps and mechanisms of salt removal.

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In one embodiment, the present invention describes the preparation of the electrode for CDI via in-situ polymerization with styrene monomer onto RGO to create a single molecular construct for electro-adsorption and selective ion permeation. Positively and negatively charged electro adsorbent-ion exchange resins (EAIERs) were synthesized with sulfonate and quaternary amine functionalities, respectively. Primarily, RGO-PS composite was functionalized by incorporating the sulfonate and quaternary amine moieties. Individual RGO sheets with such 20 selective functionalization are referred to as the molecular constructs. The covalent construct is mixed with additives including carbon nanotubes (CNTs), fullerenes and carbon fibers to enhance the performance. These EAIERs 'molecular constructs' were used as CDI electrodes and further used in desalination process for the removal of different ions.

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In another embodiment, the present invention describes the fabrication of these electrodes. The electrode material was blended along with limited quantities of polyvinylidene fluoride (PVDF) as a binder (~15 wt%), and coated on a graphite sheet which was cured overnight to make working electrodes.

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In another preferred embodiment, the present invention illustrates the assembly of electrodes, comprising chemically-linked reduced graphene oxide cationic and anionic exchange resins molecular constructs used for the removal of salt species (viz. sodium chloride (NaCl), magnesium chloride (MgCl₂), ferric chloride (FeCl₃), sodium nitrate (NaNO₃), sodium fluoride (NaF) and sodium sulfate (Na₂SO₄)) under external applied potential. It also gives insight into the mechanism of salt adsorption and desorption.

BRIEF DESCRIPTION OF THE DRAWINGS 5

Figure 1 Schematic design of a cell with integrated EAIERs (molecular construct) for capacitive deionization (CDI). The RGO sheets have -COOH functionalization. The said design comprises: RGO-ion exchange resin (+ve) molecular construct (+ve EAIERs) (1); RGO-ion exchange resin (-ve) molecular construct (-ve EAIERs) (2); spacer (3); current collector (4); graphite sheet (5); feed water

10 (6) and purified water (7).

> Figure 2 Schematic representation of a CDI set-up used for measuring CDI performance. The said comprises: a covalently integrated graphenic electroadsorbent (+ve EAIERs) (1); a covalently integrated graphenic electroadsorbent (-ve EAIERs) (2); spacer (3); current collector (4); DC power source (8) and TDS meter (9).

15 Figure 3A) UV-Vis absorption spectra of i) polystyrene (PS), ii) reduced graphene oxide (RGO) and iii) RGO-PS composite and B) Raman spectra of i) PS, ii) RGO and iii) RGO-PS composite.

Figure 4 SEMEDS of RGO-PS functionalized ion exchange resin of A) +veEAIERs (cation EAIERs) and B) -veEAIERs (anion EAIERs). The corresponding SEM EDS and elemental mapping images are shown in the inset

20 Figure 5 SEM EDS of A) anode and B) cathode (before adsorption). The SEM image and the corresponding elemental mapping images are shown in the insets. Aluminium peak came from the SEM stub.

Figure 6 Fourier transform infrared (FTIR) spectra of A) PS, B) RGO and RGO-PS, C) RGO, RGO-PS and RGO-PS-SO₃H (+veEAIERs) and D) RGO-PS, RGO-PS-CH₂Cl and RGO-PS-CH₂ - $N^{+}(CH_3)_3Cl^{-}(-veEAIERs).$

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Figure 7 Cyclic voltammetry (CV) of A) +Ve EAIERs electrode (cathode) and B) -Ve EAIERs electrode (anode) at different scan rates; C) and D) are specific capacitance vs. scan rate for both cathode and anode materials, respectively. CV potential was varied with respect to Ag/AgCl electrode using 1 M NaCl solution as the electrolyte and current was measured between working and counter electrode.

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Figure 8 Nyquist Plots of A) +Ve EAIERs electrode (the inset chart shows the magnified high frequency region), B) -Ve EAIERs electrode (the inset chart shows the magnified high frequency region); C) and D) are cyclic repeatability of +Ve EAIERs electrode and -Ve EAIERs electrode at a fixed scan rate of 50 mV/s, respectively in 1 M NaCl as the electrolyte.

35 Figure 9 Complex capacitance vs. frequency plot: desorption rate determination for A) +Ve EAIERs (RGO-PS-SO₃H) electrode and B) -Ve EAIERs (RGO-PS-CH₂ –N⁺(CH₃)₃Cl⁻) electrode; C) and D) are Bode plots for cathode and anode, respectively in 1 M NaCl electrolyte.

Figure 10 Comparison of CDI performance between covalently integrated EAIERs(RGO-PS functionalized) electrode and carbon prepared from melamine functionalized carbon nanocellulose (CMF-CNC) electrode in 610 μ S NaCl solution and the electrosorption kinetics for the integrated EAIERs and CMF-CNC electrodes are shown in the inset. The variation in potential on the electrodes with time is shown on top of the figure.

Figure 11 The adsorption capacity of a covalently integrated EAIERs electrodes with different conductivities of NaCl solution A) 450, B) 610 and C) 802 μ S as a function of applied voltage at 1.5 V; Electrode repeatability (four adsorption-desorption cycles) performances are shown in D), E) and F).

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10 **Figure 12** The adsorption capacities of a covalently integrated EAIERs with MgCl₂ and FeCl₃ at different conductivities of 450 (A and D), 610 (B and E) and 802 μ S (C and F) as a function of the applied voltage, at 1.5 V.

Figure 13 CDI performances of EAIERs using different cations (Na⁺, Mg²⁺ and Fe³⁺) with conductivities of **A**) 450, **B**) 610 and **C**) 802 μ S, respectively. Similarly, anions (Cl⁻, NO₃⁻, F⁻)

and SO_4^{2-}) with conductivities of **D**) 450, **E**) 610 and **F**) 802 μ S, respectively. Operating potential: 1.5V.

Figure 14 SEM EDS of MgCl₂ adsorption after a single adsorption cycle on A) cathode and B) anode. The corresponding SEM EDS and elemental mapping images are shown in the inset.

Figure 15 XPS survey spectra of the material after single adsorption cycle, (a) anode and (c) cathode (before adsorption); (b) anode and (d) cathode (after FeCl₃ adsorption).

Figure 16 Deconvoluted XPS spectra of Ai) Cl 2p, Aii) Fe 2p of the cathode and Bi) Cl 2p, Bii) Fe 2p of anode after the adsorption of FeCl₃.

Referring to the drawings, the embodiments of the present invention are further described.

25 The figures are not necessarily drawn to scale, and in some instances the drawings have been exaggerated or simplified for illustrative purposes only. One of ordinary skill in the art may appreciate the many possible applications and variations of the present invention based on the following examples of possible embodiments of the present invention.

30 DETAILED DESCRIPTION OF THE INVENTION

The following description is presented to enable any person skilled in the art to make and use the embodiments, and is provided in the context of a particular application and its requirements. Various modifications to the disclosed embodiments will be readily apparent to those skilled in the art, and the general principles defined herein may be applied to other embodiments and applications without departing from the spirit and scope of the present disclosure. Thus, the present invention is not limited to the embodiments shown, but is to be accorded the widest scope consistent with the principles and features disclosed herein.

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The present invention relates to the development of the CDI electrode for salt removal from brackish water. Figure 1 depicts the schematic representation of a cell with an integrated EAIERs electrode for CDI. According to the invention, the EAIERs materials were coated on the current collector (graphite sheet) and a potential was applied to drive the ions separating them from the input water using an external DC power source.

Synthesis of graphene oxide (GO) by the modified Hummer's method, which was further reduced using ammonia and hydrazine hydride [Park, S.*et al.*, Carbon, 2011, 49, 3019-3023] in the ratio of (3:1) with continuous stirring for 12 h at 95°C. After completion of the reaction, the formed reduced graphene oxide was washed with deionized (DI) water several times and dried using a freeze dryer. RGO (1 g), styrene (ST) monomer and divinylbenzene (DVB) were taken in the ratio of 10:1:0.1 in 25 mL DI water and ultrasonicated for 10 min to obtain the uniform dispersion. Polymerization process was carried out in inert condition (using N₂ gas). Typically, 1 g of RGO, 100 mg of styrene monomer and 10 mg of divinylbenzene mixture were added to 250 mL, 3 necked round bottom flask containing 25 mL of DI water. This solution was stirred for 15 min, and then 320 mg of K₂S₂O₈ was added to the reaction mixture. The reaction mixture was

- stirred at room temperature for the next 30 min and the temperature was gradually increased to 70 °C and maintained for 1 h, which was maintained at 80–85 °C for 12 h and further the temperature was increased to 90-95 °C for 2 h. After completion of the reaction, the formed RGO-PS composite was washed with hot DI water and dried overnight at 90 °C in a hot air oven.
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For making anionic EAIERs (-veEAIERs), anchoring of chloromethyl group to the network of the polymer composite (RGO-PS) is essential, for which Friedel-Craft alkylation reaction was performed. The polymer composite (1 g) and chloromethyl methylether (3 mL) were mixed in 10 mL DI water, to swell the cross-linked polymer for 2 h at room temperature. ZnCl₂ (~380 mg) was added to it and the reaction was stirred for 12 h at 35-38 °C (room temperature). The chloromethylated product was washed with acetone several times and dried for 60°C overnight. The chloromethylated product was immersed in 1,2-dichloromethane (DCM)

for 2 h to swell. Trimethylamine hydrochloride (1 g) was then added to the resultant mixture and the reaction was continued for next 6 h at room temperature. The final chloro-aminated product (or -veEAIERs) was dried at 60 °C overnight [Li, Y. *et al.*, RSC Adv., 2015, 5, 2550-2561; Li, Y. et al., J. Appl. Polym. Sci., 2015, 132, 41234/1-41234/8].

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To synthesize cationic EAIERs (+veEAIERs), RGO-PS composite (1 g) was dispersed in 20 ml of 4 M H₂SO₄ and stirred for 24 h at 100 °C. After completion of the reaction, the formed +veEAIERs were kept it in a hot air oven at 60 °C for drying [Yao, Y.F.*et al.*, ACS Appl. Mater. Interfaces, 2011, 3, 3732-3737; Li, H.Y.*et al.*,J. Membrane Science, 2014, 466, 238-245].

To assemble the electrodes, EAIERs and ~15 wt% of PVDF were dispersed in DMF solution and stirred to make a homogeneous viscous slurry. This was then coated to on a graphite sheet and kept for curing. The sheet was then immersed in deionized (DI) water overnight before performing anyexperiments. A laboratory-scale CDI batch experiment was performed by a single pair of EAIERs electrodes, as shown in figure 2. Graphite rods were used as the current collectors and the spacing between the two electrodes was maintained at~0.4 mm by using a nylon membrane.

This single electrode set-up was immersed in a 100 mL beaker containing 80 mL of saline water containing different ions at varied conductivity (450, 610 and 802 μ S). By applying a potential difference on the electrodes, the cations and anions from the feed water get adsorbed on the cathode and anode, respectively. This process will continue until the electrodes become saturated and the system attains equilibrium. The regeneration of the electrodes were done by reversing the polarity of the electrodes, where all the adsorbed ions were desorbed and the same surface was further used for next cycles. The maximum adsorption capacity of the material was calculated from the equilibrium adsorption curve. The temperature of the solution was kept constant at ~23-25 °C.

25 The electro-adsorption capacity (Q, mg/g) of the electrodes was calculated using the formula:

$$Q = (C_i - C_f) * V/m$$

Where C_i and C_f arean initial and final concentrations of the solution (mg/L), V is the volume of the solution (mL) and m is the total mass of the electrodes (in g).

The invention may be further illustrated using the accompanying diagrams.

Figure 1illustrates the designof a cell with integrated EAIERs (molecular construct) for CDI. A spacer was placed between the two electrodes. The expanded view depicts the molecular

construct of both +veEAIERs (RGO-ion exchange resin (+ve) molecular construct) and – veEAIERs (RGO-ion exchange resin (-ve) molecular construct). The basic mechanism underlying CDI is schematically depicted in figure1 (Porada, S. *et al.*, Prog. Mater. Sci., 2013, 58, 1388-1442).

- 5 Figure 2 illustrates the experimental set-up for analysing the salt adsorption-desorption in batch process. The DC power source supplies external potential to the electrodes. This potential drives the ions present in the solution toward the electrodes. A total dissolved solids (TDS) meter was immersed into the solution to measure the change in conductivity of the solution with time.
- Figures3 (Ai-Aiii) illustrate comparisonof the UV-Vis spectral features of PS, RGO and
 RGO-PS. Characteristic peak maxima at ~273 and ~287 nm for PS [Li T *et al.*, Polymer Bulletin,
 1991, 25, 211-216] were observed in Figure 3 (Ai). The characteristic peak at 277 nm in Figure 3 (Aii) corresponds to RGO. Two new peaks at~270 and ~290 nm were observed for RGO-PS composite which indicate an interaction between RGO and PS. The presence of both RGO and PS features in the spectra indicate the formation of the RGO-PS composite in Figure 3 (Aiii).
- Peaks at 846, 898, 980, 1063, 1192and 1217 cm⁻¹ correspond to the Raman spectrum of PS [Edwards, H. G. M.*et al.*, Vibrational Spectroscopy, 2000, 24, 213-224] in Figure 3 (Bi). For the RGO-PS composite, significant peaks at 973, 1007, 1105, 1141, 1317and 1577 cm⁻¹were observed. Figure 3 (Bii) illustrates Raman spectrum of RGO indicating the presence of G and D bands, which signifies sp² hybridization (graphitic signature of carbon) and disorder due to the defects induced on the sp² hybridized hexagonal sheet of carbon. Peaks at 1331 and 1580 cm⁻¹ in
- RGO are for D-band and G-band, respectively. In Figure 3 (Biii), the peak position of the Gband, corresponding to RGO-PS did not shift but the position of D-band shows a considerable shift of 14 cm⁻¹ compared to RGO, which is likely due to the polymer chains anchored to the oxygen functionalized edges of the RGO.
- Figure 4 (A) illustrates SEM EDS of +veEAIERs, which contains C, O and S as the only elements. The presence of S is due to the –SO₃group after sulfonation of EAIERs. Similarly, the SEM EDSand elemental maps of–veEAIERsareshown in Figure 4 (B) which contains C, O andsmall amount of N and Cl due to the chloro-aminated product forming–veEAIERs. Corresponding SEM images and elemental maps are shown in the inset (Figure 4).
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Figure5(A and B) illustrateSEM EDS and elemental maps are shown for the anodic and cathodic electrodes. The functionalized EAIERs along with polyvinylidene fluoride (PVDF)

which was used as a binder (~15 wt%), were coated on graphite sheet and dried to make the working electrodes. The peak for F, seen in both the cases inFigure3 is because of PVDF. Presence of N and Cl in Figure 5 (A) confirm it to be –veEAIERs and the presence of S in Figure 5 (B) confirm it to be +veEAIERs. The presence of the peak due to aluminiumin EDS is from the SEM stub.

5 SEM

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Figure 6 (A) illustrates FTIR spectrum of PS showing characteristic peaks at 3035 cm⁻¹ for the aromatic C-H stretching vibration, 2925 and 2850 cm⁻¹ correspond to the asymmetric and symmetric stretching frequency of C-H groups of aliphatic C-H, 1632 and 1450 cm⁻¹ correspond to C=C stretching and C-H deformation frequency, respectively. Figure 6 (Bi and Bii) illustrates the IR spectra of RGO and RGO-PS composite. IR spectrum of RGO has been reported elsewhere. The peaks at 2924 and 2854 cm⁻¹ for C-H stretching (asymmetric and symmetric, respectively) of RGO. The peak at ~1634 cm⁻¹ correspond to C=C stretching frequency and peak at ~1740-1745 cm⁻¹ correspond to C=O stretching of the carboxylic acid group of RGO. The

RGO-PS composite spectrum shows peaks at 2968, 2922 and 2852 cm⁻¹ that correspond to the C-

- 15 H frequency of CH2, asymmetric and symmetric stretching frequency of C-H groups of aliphatic C-H, respectively. The peak at 1631 cm⁻¹correspond to C=C stretching frequency of RGO-PS. Here, a substantial increase in the intensity of C=C is observed in RGO-PS composite which is due to the covalent linkage between RGO and PS. The spectrum confirms the formation of the RGO-PS composite. Figure 6 (Ciii) illustrates the FTIR spectrum of RGO-PS-SO₃H
- 20 (+veEAIERs).The peaks at 1224 and 1180 cm⁻¹ correspond to S=O bond of SO₃H in RGO-PS composite. The peaks at 2925 and 2852 cm⁻¹are for asymmetric and symmetric stretching frequency of aliphatic C-H of +veEAIERs. Figure 6 (Dii) indicates thatafter chloromethylation of RGO-PS composite, the product shows two prominent peaks at 1411and 1261 cm⁻¹which are attributed to the bending vibration of C–H in chloromethyl (–CH₂Cl) groups and bending
- vibration of aromatic C–H in Ph–CH₂Cl groups, respectively. Peaks at 2923 and 2851 cm⁻¹ correspond to C-H stretching (asymmetric and symmetric stretching, respectively) of RGO-PS-CH2Cl. Figure 6 (Diii) shows FTIR spectrum of RGO-PS-CH₂–N⁺(CH₃)₃Cl⁻ (–veEAIERs).After amination of the chlorinated product, new peaks appeared at ~1208and ~1154 cm⁻¹,attributed to the C–N stretching of tertiary amine group in-veEAIERs. Peaks at 2962, 2924 and 2952 cm⁻¹
- ¹correspond to C-H stretching (for CH2, asymmetric and symmetric stretching, respectively) in veEAIERs. Also, peaks at 1638 and 1632 cm⁻¹ correspond to the C=C stretching frequency of –

veEAIERs and RGO-PS-CH₂Cl,respectively. FTIR spectra confirmed these iscovalent linkages between RGO and PS, and confirm the formation of anionic and cationic EAIERs.

Figures 7(A and B) illustrate CV curves obtained at different scan rates between 1 and 1000 mV/s for cathode and anode, respectively. A noticeable change in the shape of CV curve at
higher scan rates is due to large current and increased resistance. At lower scan rates, the electrolyte penetrates into the pores of the EAIERs electrode with unrestricted motion, which helps to the formation of double layer capacitance at the interface of hierarchical surface. However, at higher scan rates, ions does not have sufficient time to penetrate inside the porous structures yielding ionic transport resistance which affects the formation of the electrical double layer in the system. Figures 7 (C and D) depict the specific capacitance vs. scan rate for both cathode and anode, respectively. CV potential varied with respect to Ag/AgCl electrode using 1 M NaCl solution as the electrolyte. The specific capacitances were found to be 38.473 F/g, 35.548 F/g, 31.928 F/g, 28.961 F/g, 26.354 F/g, 18.995 F/g, 17.066 F/g, 14..487 F/g, 12.797 F/g

and 4.514 F/g at scan rates of1 mV/s, 2 mV/s, 5 mV/s, 10 mV/s, 20 mV/s, 75 mV/s, 100 mV/s,
15 150 mV/s , 200 mV/s and 1000 mV/s, respectively, for +ve EAIERs. Also for -ve EAIRs, the specific capacitances were found to be33.115 F/g, 30.596 F/g, 27.840 F/g, 25.249 F/g, 22.813 F/g, 16.405 F/g, 14.752 F/g, 12.807 F/g, 11.364 F/g and 3.181 F/g, at scan rate of1 mV/s, 2 mV/s, 5 mV/s, 10 mV/s, 20 mV/s, 75 mV/s, 100 mV/s, 150 mV/s, 200 mV/s and 1000 mV/s, respectively.

Figures 8 (A and B) illustrate the Nyquist Plot of +Ve EAIERs electrode (expanded view is shown in insert) and -Ve EAIER electrode (expanded view is shown in insert). Electrochemical impedance spectroscopy (EIS) was performed in 1 M NaCl electrolyte solutions with frequency range between 3 MHz to 5 mHz. To characterize the interfacial transport property including electrical conductivity of the material, we studied the Nyquist plot with the help of the EIS measurement for +ve EAIERs and -ve EAIERs electrodes. As shown in Figures 8 (A and B), the Nyquist plot constitutes two regions between Z' (real axis) and Z'' (imaginary axis), corresponding to a semicircle at high-frequency and followed by a straight line in the low frequency region. In the high frequency region, first intercept of the semicircle is expressed as the equivalent series resistance (ESR), reflecting the diffusion and transport of ions in the

electrolyte [Dutta, S. *et al., ACS Sustain Chem. Eng., 2016*, 4,1885–1893]. It is well known that a Nyquist plot is divided into several regions: (1) a high-frequency intercept on the real Z (real)

axis, (2) a semicircle in the high-to-medium frequency region corresponding to the charge transfer resistance (R_{ct}), and (3) a straight line at the very low-frequency region (w) or bulk resistance (Zhang, D. *et al*, *Nanoscale*, 2012, 4, 5440–5446).

- Notably, the quasi-semicircle of the +ve EAIERs and -ve EAIERs with small arc size is 5 observed, suggesting a low charge transfer resistance. In this low-frequency region, the straight line is evident for an ideal electrical double layer capacitance and fast ion diffusion behavior resulting from low Warburg diffusion resistance. The diameter of the semicircle always indicates the polarization resistance, which reflects the charge-transfer resistance between the electrodes and the solution interface. Clearly, the diameter of the second semicircle is very small which 10 indicates the negligible charge transfer resistance of the electrodes. The x-intercept of the plots reflect the equivalent series resistance (ESR), which is related to the internal resistance, including the electrodes resistance, ionic resistance of NaCl solution and the contact resistance between the carbon material and the current collector. Hence, the +ve EAIERs and -ve EAIERs electrode have a favorable accessibility for ions. This result reflects the fact that the EAIERs 15 electrode exhibits good charge storage behavior with the electrical double layer capacitive(EDLC) mechanism. To sum up, the EAIERs electrode possesses low internal resistance and good conductivity. The EIS results demonstrate that the EAIERs electrodes have easier transport pathways for salt ions and is more suitable for CDI. In Figures 8 (C and D), Cyclic Voltammogram performed on +Ve EAIERs and -Ve EAIERs electrodes, testing their reproducibility 400 times, at a scan rate of 50 mV/s. This experiment was done with 1 M NaCl 20
- electrolyte solution in a potential window of -1.0 to 1.0 V, using platinum wire as the counter electrode and Ag/AgCl as the reference electrode.

Figure 9 illustrates the complex capacitance vs. frequency plot for the determination of desorption rate of A) +Ve EAIERs (RGO-PS-SO₃H) electrode and B) -Ve EAIERs (RGO-PS-CH₂ -N⁺(CH₃)₃Cl⁻) electrode. Figure 9 (C and D) are bode impedance plots for cathode and anode respectively, in 1 M NaCl electrolyte. It is well known that the imaginary part, capacitance *C*", corresponds to irreversible energy dissipation and represents a relaxation process during ion transport [Yoon, S. *et al.*, *Electrochim. Acta.*,2015, 50, 2255; Jang, J. H.*et al.*,*J. Electrochem. Soc.*, 2004, 151, A571; Jang, J. H. *et al.*,*J. Electrochem. Soc.*, 2005, 152, A1418]. The relaxation

30 time constants of the adsorption and desorption processes are correlated to the peak frequency

(or relaxation frequency) $f_{R,as}$: $\tau_R = 1/(2\pi f_R)$ [Huang, C. W. *et al*, *Carbon 2011*, 49, 895]. As a result, τ_R was 1.24 s for +ve EAIERs and 0.91 s for –ve EAIERs electrode. EIS was performed withvarying frequency from 3 MHz to 5 mHz (Figures 8 A, 8 B, and 9). The rate capability and ions transport through a porous electrode can be quantitatively related to the relaxation time constant. The peak corresponding to C'' was used to identify the relaxation time constants and quantitatively study the rate capability of the EDLC electrodes. The relaxation time constant increases with increasing shell thickness. Figures 9 (C and D) are the corresponding bode plots for EIS measurements shown in Figures 8 (A and B), respectively. Electrochemical characterization of electrodes indicates high conductivity, porosity and capacitance (Figures 7, 8 and 9).

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The performance of integrated CDI electrodes (EAIERs) was compared with conventional CDI carbon electrodes. The carbon powder prepared from melamine functionalized nanocelulose (MF-CNC) was used for conventional CDI (CMF-CNC). It is evident from Figure 10 that the RGO-PS-functionalized (EAIERs) electrodes have higher adsorption capacity (~15.86 mg/g)

- 15 than CMF-CNC electrodes(~7.45 mg/g) for Cl⁻ions at 610 μ S NaCl solution. In the case of EAIERs electrodes, the adsorption occurs in the first 58 min and attains an equilibrium. After 120 min, byreversing the polarity of the electrodes, desorption starts to occur. The concentration of the solution approaches the initial value of 610 μ S, as all the adsorbed ions desorb and the adsorption sites are regenerated. The electrodes remain at equilibrium till the potential is again
- reversed. Similarly, CMF-CNC electrodes were tested to compare the adsorption and desorption capacities. Theytook ~73 min to attain the adsorption equilibrium. By reversing the polarity after 120 min, desorption was observed which regenerated the adsorption sites on the electrode. Unlike EAIERs, the CMF-CNC electrodes again start to adsorb ions before all the ions are desorbed from the electrodes. This is the key difference between the two electrodes. The electrosorption kinetics for the integrated EAIERs and CMF-CNC electrodes are shown in the inset of Figure 10. The EAIERs electrodes show three different adsorption kinetics till reaching equilibrium. Initially, within the first ~11 min, the adsorption was fast, from ~11-53 min, adsorption was moderate and from ~53-64 min, the adsorption was very slow. Similarly, a CMF-CNC electrode also shows three different adsorption kinetics, initial within the ~20 min, the

30 adsorption was fast, during ~20-71min, it was slow and from ~71-80 min, the adsorption was

very slow. This shows that EAIERs electrodes have more active adsorption sites than conventional CDI electrodes during the same contact time.

The electrical adsorption capacity of the electrode material depends on: i)the thickness of ELDs, ii) hydrated ionic radii, iii) ionic charge and iv) initial concentration of the solution. To determine the abovementioned parameters for EAIERs electrodes, a set of different concentrations of NaCl, MgCl₂and FeCl₃ solution were prepared as an electrolyte and a CDI batch experiment was performed using 1.5 V DC power source (optimized). Electrochemical adsorption capacity was measured from an adsorption-desorption curve, shown in Figures 11 and 12.

- Figures 11 (A-C) illustrates the adsorption capacity of a covalently integrated EAIERs electrodes with different conductivities are shown. It was observed that with an increase in the concentrations of NaCl ions, the adsorption capacity of the EAIERs electrodes increases. The values are 14.45, 15.86 and 15.93 mg/g for Cl⁻ ions of NaCl with conductivities of450, 610 and 802 μS, respectively. The adsorption capacity values obtained are much higher compared to pristineRGO/grapheme based CDI electrodes in batch experiments reportedearlier. Adsorption-desorption performance of the electrodes is shown in Figures11 (D-F). Only four cycles of electrode adsorption-desorption are presented in the figures, but it was seen that even after ten cycles, the efficiency remains the same. Therefore, from the performance and repeatability point
- Figures12 (A-C)illustrateconductivityvs time plot up on varying the concentration of MgCl₂ ions in the solution. For the input conductivity of 450, 610 and 802μS, the adsorption capacity of Mg²⁺ ions were 20.40, 23.51 and 26.63 mg/g, respectively. Figures12 (D-F) illustrates that the adsorption capacity of Fe³⁺ ions were 28.9, 32.58 and 34.28 mg/g keeping the initial conductivity of 450, 610 and 802 μS, respectively. It was observed that in both the cases of anion and cation, adsorption capacity of the EAIERs electrode increases with increase in the

of view, our material can be used as CDI electrode for getting potable water from brackish water.

- Figures 13 (A-C)illustrate acomparison of the adsorption capacity of EAIERs for different cations having the same initial concentrations in the solution. It is evident that adsorption capacity of the material follows the trend, $Fe^{3+} > Mg^{2+} > Na^+$ for the cations keeping Cl⁻ as the anion for all the
- 30 cases. It was seen that with the increase in the charge of cations, adsorption capacity increases. Therefore, various properties such as the ionic charge, ionic radii and hydrated radii of different

cations (Na⁺, Mg²⁺ and Fe³⁺) and anions (NO₃⁻, F⁻, Cl⁻ and SO₄²⁻) are important foradsorption. For the cations, it was observed that with an increase in the valency of the metal ions, the adsorption capacity increased, but reverse trend was observed in the case of anions (keeping cation (Na⁺) as same). The hydrated radius of Fe³⁺ ion is largest compared to Na⁺ion which is smallest among

these cations. Therefore, on the basis of the above explanation, the adsorption capacity must follow the order, Na⁺> Mg²⁺> Fe³⁺but the reverse trend was observed. In the case of cations, the charge is the predominant factor than the hydrated radius. When a potential is applied on the electrodes, the cation with higher charge will be adsorbed more compared to a cation with lower charge. Therefore, trivalent Fe³⁺ionswere adsorbed at a faster rate than divalent Mg²⁺ions on the electrode surface, followed by Na⁺ions. But in case of anions, adsorption capacity decreases with increase in the charge of the anion. The adsorption capacity of the material for anions shows that CI>NO₃> F>SO₄²⁻at different concentrations [Figure 13 (D-F)]. In case of anions, hydration radii are more important than charge. The size of the hydrated radii of these anions decreases as SO₄²> F⁻> Cl⁻, NO₃⁻. Anion with smaller hydrated radius will pass through the pores and will reach the electrode surface with ease and the same trend (Cl⁻>NO₃⁻. >F⁻>SO₄²⁻)was observed.

The integrated EAIERselectrodessurface was characterized with SEM EDS and XPS after one adsorption cycle (Figures14, 15 and 16). Electrodes were kept for a long time for adsorption in MgCl₂ and FeCl₃ solutions until the equilibrium was reached. It was then washed with DI water to remove the physisorbed ions and was analyzed using SEM EDS and XPS, respectively.

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Figures14 (A and B) illustrates SEM EDS of the electrodes after adsorption of $MgCl_2$. It was observed that Mg^{2+} and Cl⁻ions were adsorbed on the cathodic and anodic surfaces, respectively. Inset of Figure 14 shows the SEM EDS and the elemental maps of the ions that were adsorbed on the surfaces.

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Figure 15 illustrates XPS survey spectra of the anodic and cathodic EAIERs electrodes after single adsorption cycle, before and after adsorption of FeCl₃ ions. In the XPS survey spectra, no significant changes in the binding energy of carbon, nitrogen, oxygen and fluoride feature corresponding to the cathode and anode were observed before and after the adsorption. The XPS survey spectra (Figure 15) and deconvoluted XPS spectra (Figure 16) show the enhanced intensity of Fe³⁺ and Cl⁻ at cathode and anode, respectively. Small amounts of Cl⁻on

cathode and Fe^{3+} onanodewere detected due to diffusion of the ions at the electrodes as they were dipped in the FeCl₃ solution.

It may be appreciated by those skilled in the art that the drawings, examples and detailed description herein are to be regarded in an illustrative rather than a restrictive manner.

We Claim:

- 1. An electrode assembly for capacitive deionization (CDI) comprising:
 - a. one electrode made of chemically-linked reduced graphene oxide-cation exchange resins molecular constructs synthesized by in-situ polymerization of styrene and reduced graphene oxide (RGO) followed by functionalization of reduced graphene oxide@polystyrene (RGO-PS) composite with sulfonate and /or carboxylate moiety;
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b. one electrode made of chemically-linked reduced graphene oxide-anion exchange resins molecular construct synthesized by in-situ polymerization of styrene and reduced graphene oxide (RGO) followed by functionalization of reduced graphene oxide@polystyrene (RGO-PS) composite with amine moiety;

wherein, electro-desorption during CDI does not lead to readsorption and consequent reduction of adsorption capacity of the overall system.

- 15 2. The electrode assembly as claimed in claim 1, wherein the resin is selected from the group of polystyrene, polysulphone, poly- acrylic acid, polyacrylamide, poly(methyl methacrylate), polyimide, polyethylene terephthalate, polyethylene grafted maleic anhydride, polypropylene, poly(vinyl alcohol), poly(vinyl chloride) and polyethylene vinyl acetate and combination thereof.
- 3. The electrode assembly as claimed in claim 1, wherein the electrode material is selected from the group of reduced graphene oxide, molybdenum disulfide (MoS_2), tungsten diselenide (WSe_2), tungsten disulfide (WS_2) and combination thereof, in general called two-dimensional materials.
 - 4. The electrode assembly as claimed in claim 1, wherein the covalent construct is mixed
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- with additives includes carbon nanotubes (CNTs), fullerenes and carbon fibers to enhance the performance.
- 5. The electrode assembly as claimed in claim 1, wherein the electrodes are used for removing salts from brackish water.
- 6. The electrode assembly as claimed in claim 1, wherein the electrodes removes cations of

- different charge including Fe³⁺, Mg²⁺ and Na⁺.
 7. The electrode assembly as claimed in claim 1, wherein the electrodes removes anions of
 - different charge including Cl^{-} , NO_{3}^{-} , F-, SO_{4}^{2-} , arsenite and arsenate ions.
- 8. The electrode assembly as claimed in claim 1, wherein positively and negatively charged ions are removed from impure water.

- 9. The electrode assembly as claimed in claim 1, wherein the adsorption and desorption occur at equal efficiency for multiple cycles.
- 10. The electrode assembly as claimed in claim 1, wherein the assembly is used along with other deionization and purification methods to enhance removal efficiency.
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Dated at Chennai this April 21, 2020

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ABSTRACT

Reduced graphene oxide@polystyrene (RGO-PS) composite was synthesized using reduced graphene oxide (RGO), styrene monomer and divinylbenzene through an in-situ polymerization process. The RGO-PS composite was functionalized with sulfonate and quaternary amine functionalities for making positive and negative integrated electro-adsorbention exchange resins (EAIERs), respectively. These EAIERs 'molecular constructs' were used as CDI electrodes and desalination was performed for the removal of different ions. A high electro-adsorption capacity of ~15.93 mg/g forCl⁻using 802µS NaCl solution was observed in laboratory
batch experiments which was much higher than the adsorption capacity of RGO electrodes reported earlier (~2-3 mg/g).

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AN INTEGRATED CDI ELECTRODE



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FIGURE 1

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AN INTEGRATED CDI ELECTRODE



FIGURE 2

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FIGURE 4

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FIGURE 5

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FIGURE 6

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150 Α В 200 100 100 50 Current (mA) Current (mA 0 1000 mV/s -50 1000 mV/s 900 mV/s 900 mV/s 800 mV/s 600 mV/s 800 mV/s 700 mV/s 700 mV/s 500 mV/s -100 600 mV/s 500 mV/s -150 _ 350 mV/s 400 mV/s-- 350 mV/s - 300 mV/s 400 mV/s – 300 mV/s -200 250 mV/s-- 200 mV/s 150 mV/s 250 mV/s -200 mV/s 150 mV/s -200 25 mV/s 100 mV/s 75 mV/s___50 mV/s 25 mV/s 100 mV/s 75 mV/s-- 50 mV/s 20 mV/s— 10 mV/s— 5 mV/s— 2 mV/s— 1 mV/s 20 mV/s— 10 mV/s-_ 5 mV/s_2 mV/s_1 mV/s -300 -250 o.o Voltage (V) Voltage (V) -1.0 -0.5 0.5 1.0 -1.0 -0.5 0.5 1.0 -)- Cathode_rgo-ps-so3h 40 D С 35 Specific capacity (C_{SD}) 35 Specific capacity (C_{SD}) 30 30 25 25 20 20 15 15 10 10 5 5 0 0 Ó 200 400 600 800 1000 200 400 1000 Ó 600 800 Scan rate (mV/s) Scan rate (mV/s)

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FIGURE 7

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FIGURE 8

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FIGURE 9

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FIGURE 10

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FIGURE 12

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FIGURE 13

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FIGURE 14

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FIGURE 15

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FIGURE 16

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