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Influence of solvent and its concentration on binding graphene with substrate in electric double layer capacitance

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ABSTRACT

EDL performances are highly influenced by the type of binder, solvent and its proportioning. The chloride removal efficiency of graphene was studied with binders like poly vinyl dene fluoride (PVdF), poly tetra fluoro ethylene (PTFE), polyvinyl pryrolidine (PVP) and polystyrene sulfonic acid (PSA). In order to fix the graphene particles properly on to substrate material solvents like water, isopropyl alcohol, N-methyl pyrolidene and dimethyl acetamide were used. The suitable type of binder and solvent was determined based on the chloride removal efficiency of graphene and the binding ability of the chosen material. Therefore PVdF and DMA are chosen as best binder material and solvent. The optimum proportion of PVdF and DMA was also determined based on electrochemical performance and stability of the electrode material. From this study, 12.5% of PVdF with graphene and 200% of DMA with PVdF is determined as optimal proportion of Binder and solvent proportion.

Keywords: EDL; Binder; Solvent; Chloride removal; Optimum proportion

1. Introduction

The tremendous growth of population challenges the task of providing adequate quantity of water to all the living being that survive on the earth. The demand for water is ever increasing leading to over-extraction of the available surface and subsurface water. This is an alarming circumstance and this can be allayed if alternate source of water is identified. Sea water is one such source, which is abundant in quantity but the presence of salt reduces the usage of this water. In order to reduce the concentration of salt and make it fit for drinking, reverse osmosis (RO) and thermal processes such as multi-stage flash (MSF), multi-effect distillation (MED) are most commonly adopted [1]. However, these technologies are able to tackle only one percent of the world's water demand and this limited contribution is due to the cost incurred in providing energy during desalination [2]. Apart from high investment, most of the existing industrial scale desalination facilities get their energy from the combustion of fossil fuels, which in turn exchange potable water for CO_2, which causes global warming [3]. Capacitive deionisation (CDI) is a promising alternative technology in desalination [4–6] due to its lower energy demand and less maintenance requirements [7].

CDI is an electrochemical method for removing salt from aqueous solutions instead of removing water from the salt [8]. This process uses a low electrical potential (0.6–2.0 V DC) to remove ions from solution by adsorbing them onto the electrical double layer (EDL) of two porous carbon electrodes [9]. EDL store electrical energy at the electrode/electrolyte interface through reversible ion adsorption. This EDL formation differentiate the charge storing capability of CDT from the conventional electrosorption process due to its high power density and increased speed of charging and discharging [10]. The charge storing capability of the CDT can be further enhanced by selecting pore geometry [11,12], doping of functional group [13] and by enlarging the specific surface area [14,15]. The increase in thickness of the EDL is due to non-faradaic effect [16].

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EDL electrodes are normally prepared as a paste or slurry with a mixture of an active material, conductive additive and a binder; which is then coated onto a substrate of good conductivity [17]. The success of EDL electrodes in desalination depends on the selection of suitable active material along with conductive additive and binder. Amidst the various carbon based active material, graphene have attracted a lot of interest because of their unique physical and chemical properties [18] like large specific surface area, high electrical conductivity and electrochemical storage. Even after,the theoretical specific surface of 2675 m^2/g is used completely, graphene can yield only a specific capacitance of 550 F/g [19]. This may be due to the fact that the pore-size distribution is equally desirable to achieve high efficiency apart from the specific surface area requirement [20].

The pore size distribution and pore size are significant factors in EDL as it affects the ease of ions mobility through the pores [21,22]. The size of the pore and the distribution of pore in the active material is highly influenced by the concentration and the type of binder solvent used to prepare the slurry of binder in the electrode fabrication. The usage of binders cannot be eliminated as it is essential to prevent the falling off active material from the substrate and to enhance the mechanical strength of the electrode [23]. The degree of dissolution of the binders in the solvent also partly determines the size and the distribution of pores of the Electrode material apart from the identification of suitable binders.

Hence in this study an attempt was made to study the effect of binder solvent and its concentration on the orientation and the size of the pores of electrode material. If suitable solvent has not been employed then the binding effect will be less which in turn affect the stability as well as the efficiency of the CDI process. The identification of suitable concentration of the binder is equally important to that of solvent as the concentration of the solvent determines the degree of dissolution. This work aims to determine the suitable organic binder along with its optimal proportion. The suitable solvent and its optimal proportion was determined based on stability and salt removal efficiency.

2. Experimental studies

The aim of this work is to determine the suitable binder, solvent and its proportion to enhance the performance of graphene as EDL electrode. First set of experimental study was carried out with binders and solvents as listed in Table 1 to determine the best binder and solvent based on reduction of chloride concentration. The second set of experimental study was carried out with various proportion of identified binders and solvent to investigate its influence on the removal of chloride.

2.1.Preparation of active material of EDL electrode

As graphene has an attractive features like high specific surface area, high conductivity and stability, to carry out the research on the influence of binder and solvent, graphene was selected as an active material. The graphene used in this study was synthesis in the laboratory from pencil graphite by electrolysis method. In this electrolysis process pencil graphite rod was connected to positive terminal and stainless steel plate was connected to negative terminal of DC power supply. 2N Ferrous sulphate was used as an electrolyte solution. Initially, 2V was applied for two minutes and then it was increased to 10 V until the graphite rod get deteriorated. This applied electricity attracts the charged ions and forces them in between the layers of graphite and thus interpolation occurs. Due to the heat energy the ionic particles gains more kinetic energy which in turn exerts pressure over the bonding between the layers. This pressure separates the layers of graphite into graphene.

In order to separate the graphene from the electrolytic solution, vacuum filtration was done. The filtered particles consists of both graphene and iron oxide as by-product of electrolysis since ferrous sulphate was used as electrolytic solution. The iron oxide mixed with graphene was separated by washing the filtered material in acetic acid solution and the same was washed with deionized water until the pH reaches neutral. The product thus obtained was not observed to be pure since it contains some flakes of graphite. Hence to finish off the product, the synthesized graphene was then dispersed in the solution of acetone and deionized water. The dispersed solution was kept in sonicator for an hour. After sonication, the brown dispersed solution turns into black indicating the presence of Nano graphene powder in the solution. The solution was then filtered and dried to produce powder.

2.2. Selection of binder and solvent

Numerous attempts have been carried out so far related to improvement of the capacitance of the EDL electrodes with various binders and solvent. It was clear from these studies that the binder and solvent do affect the performance of the EDL Electrode, the binders and the solvents used in this study was selected based on these work [16,24]. The proportion of the selected binder to the active material varied in the range 12.5–50% and the proportion of the binder and solvent were kept as 200, 400, 600 and 800%. The list of binder, solvent and the ratio of their proportioning used in this study is tabulated in Table 1.

2.3. Fabrication of electrode

In the present work, the factors which determines the efficiency of graphene electrode was identified as four and the levels in which these factors varies was kept as four as presented in Table 1 [25]. In the studies carried out to determine the best binder and solvent the ratio of binder to graphene was kept as 25% and the ratio of solvent to binder percentage was kept as 400. The no of experimental runs carried out to determine the best binder and the solvent was tabulated in Table 2.

Hence 16 pairs of electrodes were fabricated to carry out the experimental studies. All the electrode were fabricated using copper plate of size 5×5 cm as substrate. The substrate was first soaked in acetone solution and then in distilled water in order to remove the impurities. The required amount of suitable binder was dissolved in appropriated solvent of required quantity as listed in Table 2. Subsequently, 160 mg of graphene was dispersed into the binder

Table 1
List of binder, solvent and its proportioning

S. No	Binders	Solvent	Binder %	Solvent %
1.	Polystyrene Sulfonic Acid - PSA	Water-W	12.5	200
2.	PolyVinyl Pryrolidine - PVP	N-Methyl Pyrolidine NMP	25	400
3.	Poly Vinyl dene Fluoride - PVdF	Dimethyl Acetamide DMA	37.5	600
4.	Poly Tetra Fluoro Ethylene - PTFE	Iso Propyl Alcohol IPA	50	800

Table 2
Experimental plan to determine the best binder and solvent

Experimental Run	Binder	Solvent
1	PSA	W
2	PSA	NMP
3	PSA	DMA
4	PSA	IPA
5	PVP	W
6	PVP	NMP
7	PVP	DMA
8	PVP	IPA
9	PVDF	W
10	PVDF	NMP
11	PVDF	DMA
12	PVDF	IPA
13	PTFE	W
14	PTFE	NMP
15	PTFE	DMA
16	PTFE	IPA

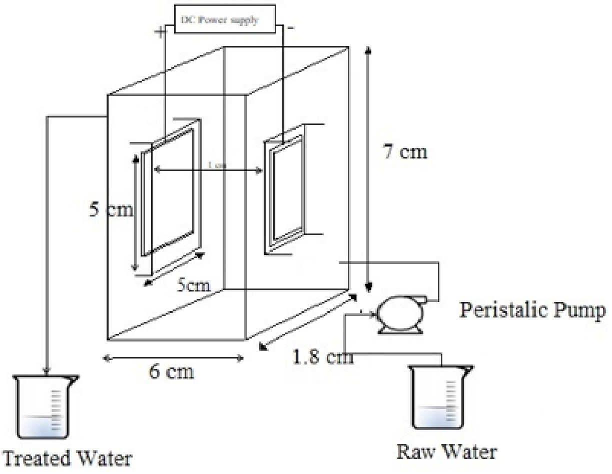


Fig. 1. Experimental setup of CDI cell.

solution and the paste thus prepared was coated on the copper substrate using doctor blade set. The coated electrodes were dried in vacuum oven at 80°C for 24 h [17].

2.4. Reactor set up

The bench scale CDI unit used for this study was designed as a flow by device with a single pass mode. The reactor was made up of acrylic material and provisions were made to insert the electrodes leaving a gap of 1 cm between the electrodes and the experimental setup used in this study is shown in Fig 1. The raw waste water containing chlorides was then pumped into the reactor at a rate of 6 ml/min using peristaltic pump. The treated sample was collected from the top nozzle at the time interval of 5 min until the concentration of chlorides in the raw waste water remains constant. The chlorides concentration present in the sample water was determined as per the standard procedure IS 3025 Part 32 [26].

3. Results and discussion

3.1. XRD analysis of synthesized Graphene

Normally graphene was synthesized from graphite by mechanical exfoliation, chemical exfoliation and liquid phase exfoliation. Mechanical exfoliation yields high quality graphene but this was not feasible option for the large scale production as reported in Sutter et al., Liang et al., Berger et al. and Su et al. [27–30]. Becerril et al. and Su et al. report that synthesis of graphene by liquid phase exfoliation damages the honey comb lattices of graphene which results in higher resistance and lesser conductivity [30,31]. An attempt was carried out to synthesize graphene by Hummers method. In the Hummers method, only 0.1 mg of graphene was successfully synthesized from 1.5 g of graphite. To carry out this study 160 mg of graphene was required to fabricate one electrode and hence in order to fabricate 16 electrodes nearly 5 g of graphene was needed. These flaws necessitates the need of a method in which these drawbacks were tackled and electrochemical exfoliation was identified as one such method of synthesis as reported by Su et al. [30]. In order to synthesize the graphene in large scale without comprising the quality, electro chemical exfoliation was carried out in this study. Nearly 2 g of graphene was synthesized in this method from a 60 × 5 mm graphite rod and the quality of graphene thus synthesized was characterized using XRD analysis. The XRD pattern thus obtained is shown in Fig. 2.

Selvam et al. synthesized graphene from graphite foil by electrochemical method. They used poly sodium diphenyl sulfonate as electrolytic solution and the synthesized material was analysed in XRD. They got the peak values at 26.35° (001 plane) and 54.30° (004 plane) [32]. In this study, the peak at the diffraction angle was observed to be 26.4° at the (002) plane and the other peak at 54.8 at (004) was obtained as shown in Fig 2. Hence by comparing this 2θ with Selvam

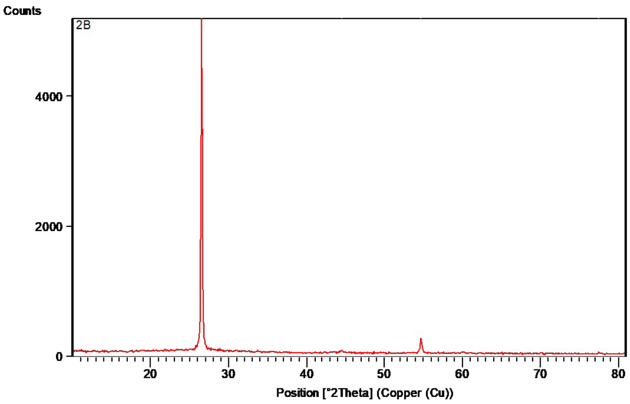


Fig. 2. XRD analysis of electrochemically exfoliated Graphene.

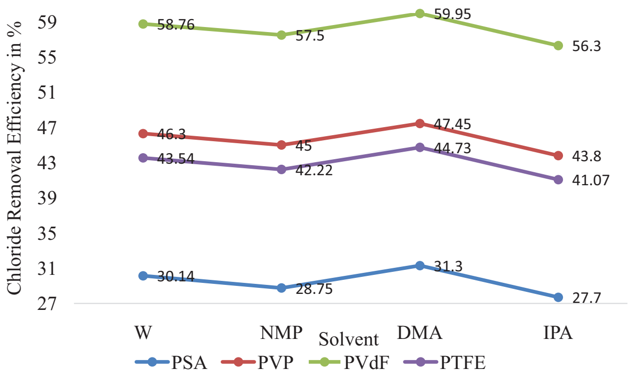


Fig. 3. Variation of chloride removal for the selected binders and solvents.

et al. work it may be concluded that the peak thus obtained indicates the crystalline nature of graphene and the peak values are well correlated with hexagonal structure with p63/mmc (194) space group (JCPDS #411487).

3.2. Effect of binder on chloride removal

This study was carried out to investigate whether the binder really affects the chloride removal efficiency of graphene electrode. Four frequently used binders were chosen and it was made as paste with various solvents. The ratio of binder to solvent was kept as 400 and the ratio of binder: graphene was kept as 25. The slurry was prepared with 160 mg of graphene mixed with the fixed amount of selected binder and solvent. The paste was then casted on the copper plate using doctor's blade set. The casted electrode was dried in vacuum oven at 80°C for 24 h. The fabricated electrode was inserted into the CDI unit and the performance assessment of each fabricated electrode was carried out. Fig 3 shows the chloride removal percentage of selected binders with different solvent. The usage of different binders do affect the removal efficiency of chloride and the highest percentage removal of chloride is shown by PVdF binder. The least percentage removal is shown by PSA binder.

Graphene as an active material shows higher percentage removal of chloride with PVdF as binder irrespective of the solvent. The maximum percentage removal of chloride with PVdF is 48% higher than PSA, 25% and 21% higher than PTFE and PVP respectively. This may be due to specific capacitance of 160.6 Fg^{-1} shown by PVdF than the specific capacitance of 121.4 Fg^{-1} by PTFE binder as reported in Zhu and Tang et al. [23]. The specific capacitance is a significant factor in determining the removal efficiency of the EDL electrode as it removes ions from the solvent through adsorption-desorption mechanism.

3.3. Effect of solvent on chloride removal

The influence of solvent on the chloride removal efficiency of the graphene was investigated through this study. From the study on the effect of binder, it is found that PVdF shows higher removal efficiency than the other selected binders. Hence PVdF was mixed with the solvents in the ratio of 1:400 to make it as slurry. The slurry was then mixed with 160 mg of active material and the paste thus prepared was coated on copper substrate using doctor's blade set. Then CDI tests were carried out to assess the effect of solvent on the chloride removal of graphene.

The chloride removal efficiency of graphene and PVdF binder along with the selected solvents is depicted in Fig. 4. From the graph it is clear that the type of solvent have less significant effect on the removal of chloride. Amidst the selected solvents, DMA shows a higher percentage removal of 59.95%. For all the solvent, the equilibrium stage is attained at 25th min except Water. After 25th min, the concentration of chloride remaining in the water starts increases and this may be due to the deterioration of the coated active material. This deterioration is observed during the experimental run and the same is shown in Figs. 5a and 5b.

The difference in highest removal percentage of chloride between DMA and Water is only 1.19%. The adsorption capacity of the electrode depend on wettability [21,22] and solubility of binder in solvent. Since the contact angle of water on PVdF is 68.7° [24] the wettability property of water is higher than DMA, which results in efficiency equal to that of DMA. In the stability point of view water exhibits lesser capacity as the hydrophilicity increases the swelling softens the PVdF which in turn reduces its strength and stability [33] of attachment electrode material on substrate. On the other hand, the Hildebrand solubility of PVdF in DMA is greater than of PVdF in water as δ_H of water is 28 $MPa^{1/2}$ and δ_H of DMA is 22.7 $MPa^{1/2}$ [34].Lesser solubility results in non uniform thickness of coating over the substrates which also reduces the strength and stability of electrodes as shown in Figs.7a and 7b.

3.3. Effect of binder: solvent proportion

PVdF polymer is made of lengthy chained molecule of CF-CH [24]. In order to make CDI as an efficient desalination process, carbon particles has to be properly fixed by binder proportion [35]. Proportioning of binder is significant as PVdF is essential for suppressing the faradaic reaction which commonly occurs with carbon particles [36]. Hence this study was carried out in order to investigate the effect of proportioning of binder and Solvent on the removal of chloride using graphene. The results obtained from this study is shown in Fig. 8.

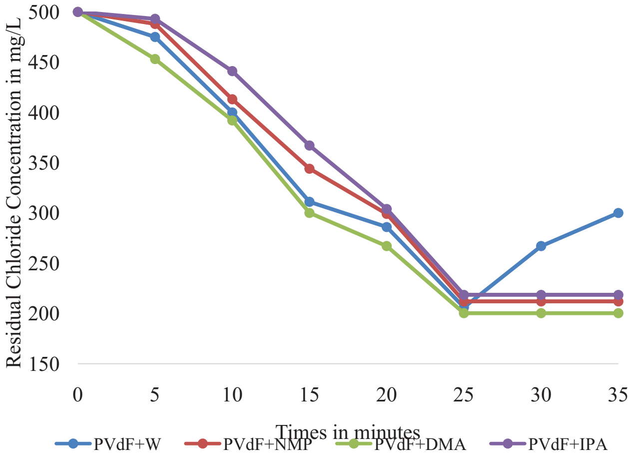


Fig. 4. Variation of chloride removal of PVdF with different solvents.

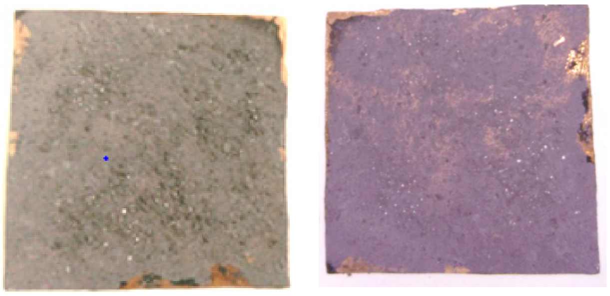

(a) (b)

Fig. 5. (a) PVdF + Water before CDI. (b) PVdF + Water after CDI.

Fig. 6. Deterioration of electrode material during CDI.

From the graph it is clear that as binder proportion increases the removal efficiency of graphene decreases. The decrease in removal efficiency with increase in PVdF concentration may be due to reduction in the mobility of ions through pores as PVdF occupy the pores of graphene [22] as depicted from the sem images of Graphene alone and Graphene with 25% PVdF and 400% of DMA shown in Figs. 9a and 9b.

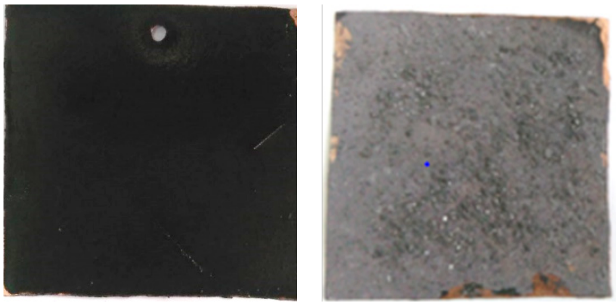

(a) (b)

Fig. 7. (a) Electrode coated with PVdF + DMA, (b) Electrode coated with PVdF + W.

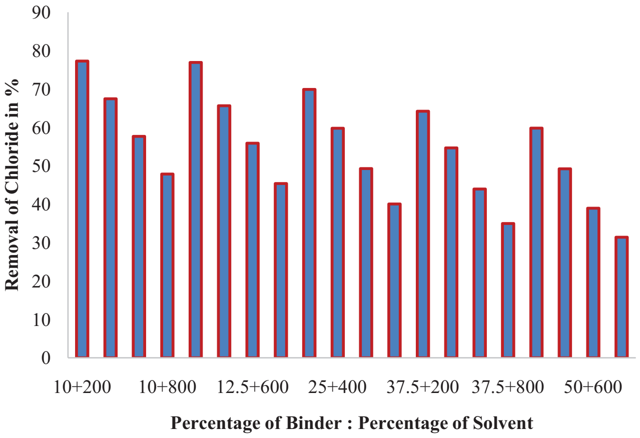


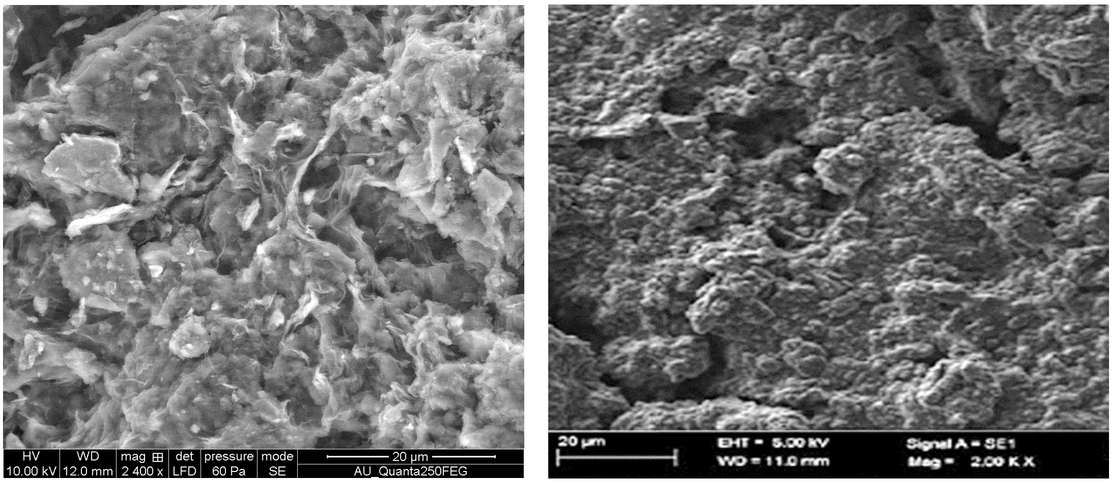
Fig. 8. Variation of chloride removal efficiency with different proportions of PVdF and DMA.

This occupancy of PVdF reduces the specific capacitance of Activated Carbon from 160.6 F/g to 125 F/g when PVdF concentration increases from 5% to 20% as determined by Zhu et al. On the other hand as PVdF concentration decreases the removal efficiency increases but we find difficulty in casting of electrode with uniform thickness. The casting of electrode with lower binder proportion results in improper binding and it shows some adhesion at initial stage. Later on when it is washed with water the coated material was stripped off. The casted electrode at initial stage and latter stage for 10% binder with 200 solvent percentage is shown in Figs. 10a and 10b.

The results shows that irrespective of binder proportion, the percentage of solvent also influences the removal efficiency of graphene. The increase in solvent proportion increases the mechanical strength which in turn reduces the capacitance of graphene [32].

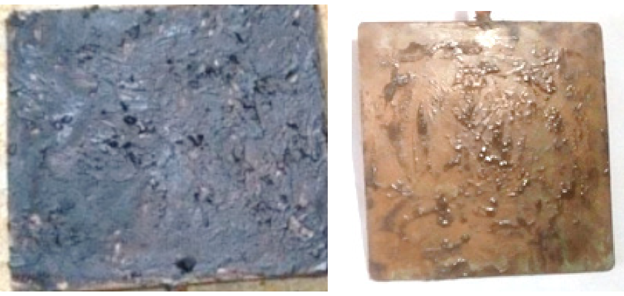
3.4. Electrosorption isotherms

Hou et al. in their research work highlighted that the saturation of surface area by the ions reflects the true ion sorption phenomena in capacitive deionization than the BET surface area [38]. Hence in this work an attempt was made to determine the saturation surface area of chloride



(a) (b)

Fig. 9. (a) SEM image of graphene without binder, (b) SEM image of graphene with 25% PVdF and 400% DMA.



(a) (b)

Fig. 10. (a) Electrode casted with 10% PVdF + 200% DMA at initial stage, (b) Electrode casted with 10% PVdF + 200% DMA after washing with water.

ions on graphene. The maximum saturation surface area and the minimum saturation surface area occupied by the chloride ions was determined. The saturated surface area occupied by the chloride ion on graphene was calculated by multiplying the adsorption capacity of graphene, Avogadro's number and the area of chloride ion based on its hydrated radius as stated by Gabelich et al. and Xu et al. [39,40]. The maximum sorption and minimum sorption capacity of graphene was determined by carrying out the isotherm studies. From the previous studies the best binder and solvent was identified as PVdF and DMA. The best proportion and the least proportion of binder and solvent was identified as 12.5:200 and 50:800. In order to determine the maximum and minimum sorption capacity, batch studies were conducted with these two proportions of binder and solvent coated on the copper plate of 5 × 5 cm. The electrodes were kept in the provisions made in the reactor set up as shown in Fig. 1. The raw waste water containing 500 mg/L of chlorides was filled in the reactor and the treated sample was collected from the top nozzle at the time interval of 5 min until the concentration of chlorides in the raw waste water remains constant. The chlorides concentration present in the sample water was determined as per the standard procedure IS 3025 Part 32 [26]. The chloride concentration remaining in the solution was used to plot the Freundlich isotherm for best proportion and least proportion showing higher and lesser quantity of chloride removal from water is shown in Fig. 11.

Similar to Freundlich isotherm, Langmuir isotherm were also plotted for the best and least proportion showing higher and lesser chloride removal efficiency as in Fig. 12.

From the graphs shown in Fig. 12 based on the R^2 values, it may be concluded that the electrosorption of chloride on graphene follows Freundlich isotherm. Then from Freundlich isotherm the maximum and minimum adsorption capacity was determined as 0.0108 moles/g and 0.00443 moles/g respectively. The hydrated radii of chloride ion was taken as 3.31 A° [38] after which the maximum saturation surface area and the minimum saturation surface area occupied by chloride ions on graphene was calculated as 2248.43 m^2/g and 918.08 m^2/g respectively. These values are approximately 85% and 35% of specific area of commercially available graphene. Using graphene as active material in this study, the maximum removal efficiency obtained with PVdF and DMA of 12.5 : 200 was 76.9% and the minimum removal efficiency obtained with 50:800 was 31.4%. In order to compare the obtained efficiencies with the commercial available activated carbon (AC) with the same boundary conditions, another CDT study was carried out. Two pair of electrodes were fabricated with activated carbon. The slurry for the first pair of electrodes were prepared with 160 mg of activated carbon as active material with 12.5 % of PVdF as binder and 200% of DMA as an organic solvent as shown in Figs. 13a and 13b.

The second pair of electrodes were prepared with 160 mg of AC as an active material with 50% of PVdF as binder and 800% of DMA as an organic Solvent as shown in figure above. Then CDT study was carried with the same reactor set up as shown in Fig. 1 and with the same experimental

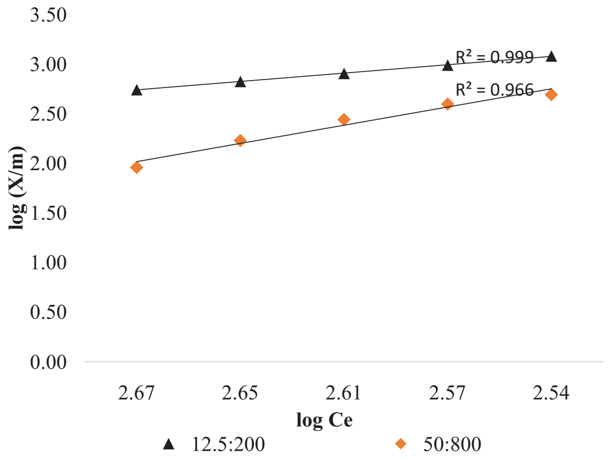


Fig. 11. Freundlich electrosorption isotherm for 12.5:200 and 50:800 proportion of PVdF and DMA.

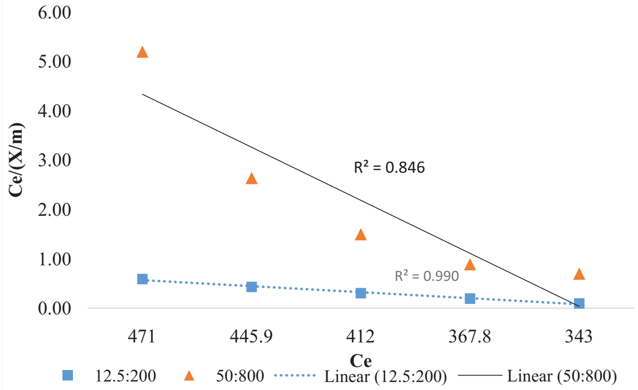
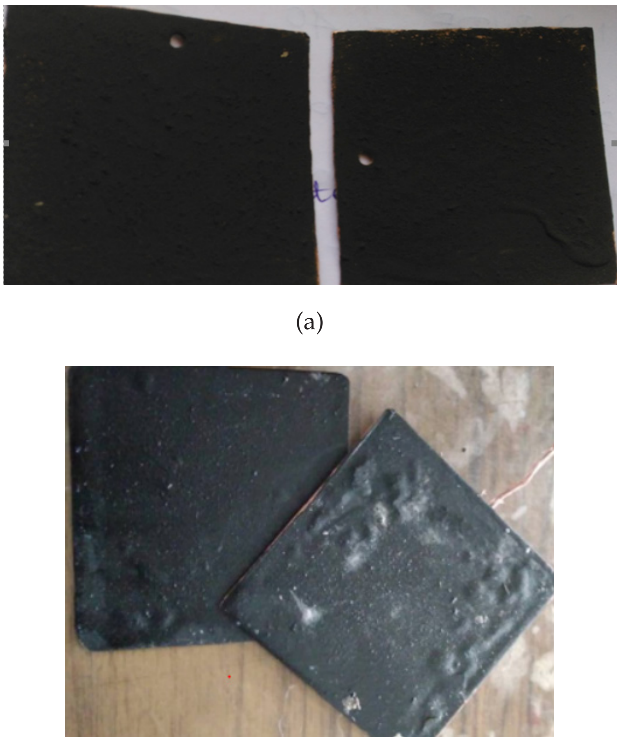


Fig. 12. Langmuir electrosorption isotherm for 12.5:200 and 50:800 proportion of PVdF and DMA.



(a)

(b)

Fig. 13. (a) Activated Carbon coated electrode with 12.5 : 200 of PVdF and DMA, (b) Activated Carbon coated electrode with 50 : 800 of PVdF and DMA.

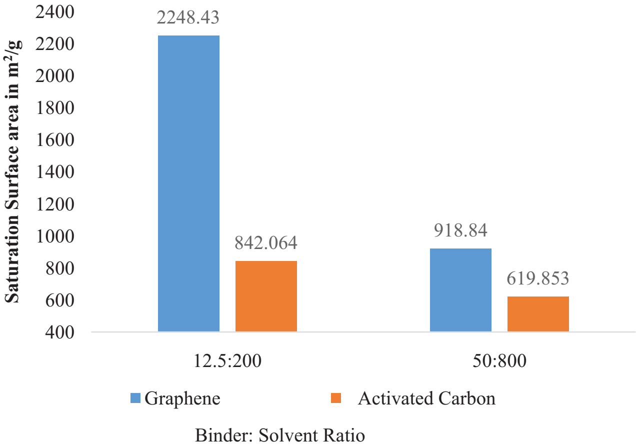


Fig. 14. Variation of saturation surface area of AC and graphene for different binder: solvent ratio.

conditions as explained in section 2.4. The treated sample was collected from the top nozzle at the time interval of 5 min until the concentration of chlorides in the raw waste water remains constant. The chlorides concentration present in the sample water was determined as per the standard procedure IS 3025 Part 32 [26] and the maximum and minimum chloride removal efficiency obtained during this study was 50% and 21% respectively. In order to find the maximum and minimum saturation surface area occupied by the chloride ions on Activated Carbon, isotherms studies were carried out as like the isotherm studies conducted with graphene. The Langmuir isotherm and Freundlich isotherm was plotted for AC with 12.5:200 and 50:800 of PVdF and DMA and from the results it may be concluded that the electrosorption of chloride ions on AC also follows Freundlich isotherm. The maximum and minimum adsorption capacity of chloride ions on AC was determined as 0.0041 mole/g and 0.003 mole/g respectively. With these values the maximum and minimum saturation capacity of chloride ion was calculated as that done for graphene and it is shown in Fig. 14.

From Fig. 14 it may be concluded that the maximum saturation surface area occupied by chloride on graphene is 65% more than the AC and minimum saturation surface area is 33% more than AC.

4. Conclusion

This study aims to investigate the influence of binder type and solvent type along with its suitable proportion on the removal of chloride using graphene as active material. Based on the research work, two hydrophobic binders like PVdF and PTFE and two hydrophilic binders like PSA, PVP were selected for this study. Water, isopropyl alcohol, N-methyl pyrolidene and dimethyl acetamide were chosen as solvent. The chloride removal efficiency of PVdF binder is commendable than PVP as PVdF comprises of lengthy CF-CH chain. The fluoride has tendency to suppress the faradaic current thereby the solubility of calcium, magnesium, chloride and hydroxyl ions increases. The influence of solvent on the chloride reduction is less significant but it have high effect on the stability of the electrode coating. The difference in removal efficiency of DMA and water is only 1.19% and hence best solvent is not determined based on chloride removal efficiency rather it is chosen based on stability. Hence PVdF and DMA is selected as suitable binder and solvent to combine with graphene on the removal of chloride. The proportioning of binder and solvent with active material do influence the performance of graphene. When the binder concentration is lower the removal efficiency was high and the binding is not proper and stable. With the increase in binder proportion the efficiency decreases as it reduces the pore size of graphene. The increase in solvent proportion increases the mechanical strength which in turn reduces the capacitance of graphene.

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