1. Introduction

Water is an indispensable commodity for the sustenance of all living organisms. It is utilized for many functions which include domestic, agricultural and industrial applications. The industrialization and urbanization are gaining momentum in all developing countries at the cost of environmental degradation. Industrial wastewater often contains higher metals along with other anions and treatment is necessitated in parliamentary procedure to avoid water contamination. Heavy metal contamination of varied water resources is of immense concern considering the toxic effect on human beings and other living organisms in the environment. Nickel is one of the major contaminants found near industries producing stainless steel, non-ferrous alloy and super alloy. Nickel and its salts are used as catalysts, in electroplating, in Ni-Cd batteries, coins, welding products and certain pigments and electronic goods. As reported by WHO, the standard limit for nickel in potable water is 0.02 mg/l.

Reverse Osmosis (RO), a membrane separation technique is extensively used to remove heavy metal ions from several industrial effluents. RO membranes are highly efficient in removal of heavy metal contaminants, but the operation has a very small water flux that requires high pressure and significant amount of energy, which attributes to the small pore size of membrane. Microfiltration and
ultrafiltration membranes with larger pores provides higher
water fluxes but they are unable to retain metal ions due to
their small size.

Nanoparticle doped Mixed Matrix Membrane (MMM)
is gaining considerable interest amongst the researchers
today. MMMs can be made to specifically remove target
contaminants and they improve mechanical, thermal,
magnetic and electrostatic properties and intensify solute,
diffusivity, selectivity, anti-bacterial property and lower
flux decline. Cellulose Acetate (CA) and its derivatives
have widespread application as a polymer base material
to cast a membrane due to its biocompatibility, non-
toxic, low cost, hydrophilic and antifouling properties.
Zero valence iron nanoparticles have been used to treat
contaminated ground water sources to remove various
metals. Recent investigations have shown that heavy
metals including arsenic, lead, chromium, cadmium,
uranium, molybdenum and mercury also can be reduced
by ZVI nanoparticles. This paper aims at the removal
of nickel from water using Cellulose Acetate doped with
Zero Valent Iron nanoparticle mixed matrix membrane.
A detailed work was carried out 1. To characterization
of the mixed matrix membrane, 2. To determining the
removal efficiency of nickel under varying concentrations,
contact time and adsorbent dosage and 3. To study
the adsorption of nickel on the surface of membrane by
adsorption isotherms.

2. Materials and Methods

2.1 Materials
The chemicals and reagents used were of analytical grade.
Ferric chloride and sodium borohydride are used to
prepare the ZVI nanoparticles. Cellulose acetate (39.8%
acetyl content; MW~30000), Acetone (Density 0.791 g/
ml) and formamide (Density 1.13 g/ml) were used to
prepare the membrane casting solution. Nickel chloride
hexahydrate was used for preparing synthetic solution of
nickel.

2.2 Synthesis of Zero Valent Iron (ZVI)
Nanoparticles
ZVI nanoparticles were prepared by the reduction of
ferric iron (Fe-III) with sodium borohydride in aqueous
medium. Uniform volumes of 0.94 molar NaBH₄ and
0.18 molar FeCl₃ were used to prepare ZVI nanoparticles
according to the following reaction

\[ 4\text{Fe}^{3+}(aq) + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow 4\text{Fe}^{0}(s) + 3\text{H}_2\text{BO}_3^- + 12\text{H}^+(aq) + 6\text{H}_2(g) \]

The ZVI nanoparticles formed were collected using
0.2 µm filter papers through vacuum filtration. The
synthesized ZVI particles are then bathed numerous times
using deionized water and ethyl alcohol before use and
stored in deionized water containing 5% ethyl alcohol.

2.3 Synthesis of Cellulose Acetate Nano-
composite Membranes
Cellulose acetate nano-composite membranes was
synthesized by phase inversion method. Cellulose acetate,
acetone and formamide was uniformly mixed to form a
homogeneous mixture and then introducing nanoparticles
into it. As shown in Table 1, two compositions CA1 and
CA2 as shown in Table 1 were prepared without adding
nanoparticles and another two CA1-Fe and CA2-Fe
compositions were prepared by adding nanoparticles.
The viscous mixture was poured onto a glass plate and
drawn manually using a bar coater with a fixed gap of 150
µm forming a thin film of membrane. Immediately after
casting the glass plate was put in ice cold deionized water
for 2 hours.

| Composition of casting solution of CA nano-composite membrane |
|---------------------------------------------------------------|
| Casting solution (g/wt %)                                       |
| Membrane | CA1 | CA2 | CA1-Fe | CA2-Fe |
| Cellulose acetate | 17.0 | 17.0 | 17.0 | 16.8 |
| Acetone | 49.0 | 61.0 | 49.0 | 48.5 |
| Formamide | 34.0 | 22.0 | 34.0 | 33.7 |
| Iron nanoparticles | 0 | 0 | 1.0 | 1.0 |

2.4 Characterization
SEM analysis was conducted separately for ZVI
nanoparticles and CA1-Fe and CA2-Fe membranes to
study their surface morphology. Elemental analysis and
their percentage was detected using Energy Dispersive
X-ray spectroscopy (EDX analysis).

2.5 Adsorption of Nickel
Batch experiments was conducted for the study of
adsorption of nickel by the membranes. Stock solution
of nickel of concentrations 20, 40, 60, 80, 100 and 120 mg/l was prepared. A piece of membrane of weighing 1 g was put in the solution. The solutions were kept in an orbital shaker at 150 rpm and at room temperature i.e. 25°C and later analyzed. The quantity of solute ($q_e$) adsorbed was determined from mass balance and a graph was plotted against equilibrium concentration to find the desired isotherm. pH study was conducted by adding HCl or NaOH(sol), of 0.1 N strength to the solutions in appropriate amounts.

### 2.6 Adsorption Isotherm

Adsorption isotherm is the inter-relation between adsorbent and adsorbate and is mostly useful for the design of adsorption process. Langmuir and Freundlich isotherms models along with other isotherm models are used to interpret the experimental data of adsorption. The adsorption isotherms at equilibrium are depicted by plotting solid phase concentration ($q_e$) against liquid phase concentration ($C_e$) of solute in the solution.

### 3. Results and Discussion

#### 3.1 Characterization

The morphology of ZVI nanoparticles was studied by SEM as shown in Figure 1(a). The ZVI nanoparticles are seen in structure of nanospheres, which exist in contact with each other and form chains. The magnetic properties of iron species suggest the linear orientation. The lighter regions are mainly on the surface of the particle and the darker regions are confined in the center of the particle. The core is formed of metallic iron and the shell (surface) is composed of iron oxides. The morphology of CA membrane by SEM as depicted in Figure 1(b),(c). CA1-Fe shows less porosity and CA2-Fe is more porous, which clearly indicate that an increase in acetone increases porosity and also enhances hydrophilicity of the membrane. EDX spectroscopy determined the elements and their percentage in the ZVI nanoparticles as depicted in Figure 1(d). The amount of iron was found to be 81.74 by weight % and 56.18 by atomic %, whereas oxygen found to be 18.26 by weight % and 43.82 by atomic %. The presence of oxygen corresponds to the reacted iron present on the surface leading to the formation of iron oxide.
Removal of Nickel by Adsorption from Aqueous Solution by Cellulose Acetate-Zero Valent Iron Nanoparticle Mixed Matrix Membrane

3.2 Effect of Nanoparticles
All the membranes prepared were tested for removal efficiency of nickel from aqueous solution by vacuum filtration. Feed concentration of 50 mg/l was allowed to pass through the membrane placed in the micro filtration flask attached with a vacuum pump. The residual concentrations of the ions were analyzed using LaMotte smart spectrophotometer. It was found that ZVI nanoparticles highly influence the removal of nickel from the aqueous solution. The maximum removal efficiency of nickel was about 73% for CA1, 83.5% for CA2 and 89.52% for CA1-Fe membrane and 96% for CA2-Fe membrane.

3.3 Effect of pH on Removal Efficiency and Concentration of Contaminants
The removal of nickel is observed to be maximum within the pH range of 5-7 as shown in Figure 2, which contributes to the partial hydrolysis of ions. An increase in pH, i.e. above 8 leads to precipitation of ions on the adsorbent surface by formation of Ni(OH)₂ compounds.

The effect of initial concentration of ions on the adsorption rate was studied in the rage (10-100 mg/L) for 2 hours contact time. From the Figure 3 it is observed that the initial concentration affects the removal and the removal percentage tends to decrease with increase in initial ion concentration. The reason for the trend can be, at higher metal concentration, due to the increased ratio of initial number of moles of the ion to the vacant sites available, efficiency reduced. Therefore, it was evident from the results that ion adsorption was dependent on the initial ion concentration.

3.4 Effect of Dosage of Adsorbent and Contact Time of Adsorbent
It is evident from the Figure 4 that the removal of ions increased with an increase in the adsorbent dosage for both the adsorbents. This is to be expected because for a fixed initial solute concentration, increase in total adsorbent doses provides a greater surface area or adsorption sites and increases the adsorption potential.

Adsorption studies were conducted with CA1-Fe and CA2-Fe membranes at 27°C by varying the stirring time from 15 to 200 minutes. It was observed that during first 75 minutes the removal of contaminants was increasing sharply and reached equilibrium and then no significant removal of ions was noticed. After 90 minutes the rate of adsorption slowed down and it started to decline as shown in Figure 5.
3.5 Adsorption Isotherms

Various isotherms for nickel were plotted using the batch study and are shown in Figure 6 and Figure 7. From the isotherms, it can be observed that for CA1-Fe Langmuir fits the best with regression coefficient of 0.998 and CA2-Fe Freundlich fits the best with regression coefficient of 0.9963 showing physisorption and chemisorption respectively.

4. Conclusion

In this study, cellulose acetate membranes were prepared with and without Zero Valent Iron nanoparticles, which were used for the removal of nickel ions. Influence of process parameters such as pH, contact time, adsorbent dosage, initial metal ion concentration and their effect on the removal efficiencies of the ions was studied using membranes with nanoparticles. The major conclusions drawn from this study are as follows.

- The maximum removal efficiency of the nickel was about 96% for CA1-Fe membrane.
- The best pH of the solution for contaminants removal was in between 5 and 7.
- Initial concentration of metal ion has shown the retarding effect on adsorption efficiency i.e. at lower levels the adsorption was higher.
- The minimum dosage for removal of nickel was found to be 0.4 grams and the required contact time for batch process was 75 minutes.
- Nickel obeys Langmuir in case of CA1-Fe and Freundlich adsorption isotherm in case of CA2-Fe.

5. References

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