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Removal of Manganese from wastewater by using Micellar Enhanced Ultrafiltration (MEUF)

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Abstract**-- Micellar Enhanced Ultrafiltration (MEUF) was used to remove Mn^{2+} from wastewater efficiently. 10 kDa Polysulfone membrane was used to obtain ≥ 97% rejection. The effect of some important parameters were investigated, including operating time, feed flow rate, surfactant to metal (S/M) ratio, feed concentration, pH. The effect of anionic surfactant on the efficiency of Mn^{2+} removal was also studied. The influence of input variables on permeate flux and rejection efficiency of Mn^{2+} ion without surfactant (anionic), in presence of surfactant was studied. Distribution coefficient and micellar loading were also estimated to confirm the reproducibility of the results.**

Keywords**-- MEUF, Managanese, SDS, S/M ratio, Waste water**

I. Introduction

Heavy metal ions are pollutants of considerable concern because they are highly toxic and, obviously, non-biodegradable, so that their disposal as waste is dangerous for human health. Accumulation of heavy metal in the body causes serious problems such as cancer or damage to brain and nerve system. Therefore, contamination of water or groundwater with heavy metal ions is a serious problem (National Research Council, Smith 1972).

Manganese in water can affect human, aquatic life and some material (Abrams *et al.*1977, Hine and Pasi , 1975, and Suzuki, 1970). For aquatic life, high level of manganese of more than 10mg/L will be toxic. For human beings, some research has been done to relate high concentration of manganese with brain damage and neural problem (Donaldson and Barbeau, 1985). It causes Parkinson's disease which is a neurological disorder that affects movement, muscle control, and balance (Cotzias *et al.*, 1971). To control the Manganese concentration in the waste effluent, the United States Environmental Protection Agency (USEPA) has established a maximum allowable limit of 0.05 mg/liter for Mn in surface water (World Health Organization, 2006).

Many methods were developed in past to remove manganese from aqueous solution but removal of Mn^{2+} using MEUF found to be an efficient technology.

Methods like Adsorption (Nassereldeen *et al.*, 2009), filtration, precipitation (Dal Bosco *et al.*, 2006 and Wensheng *et al*., 2010), oxidation (Barragán and Cruz, 2010), RO and NF (Zheng *et al*., 2001), UF with adsorption (Han *et al.*, 2005) were developed with high efficiency of separation of Mn^{2+} from wastewater stream, but these can be implemented at only higher concentration of Mn^{2+} (> 10ppm). In this work, MEUF was used competitively to remove Mn^{2+} where low concentration of Mn^{2+} present in aqueous solution.

In MEUF, the micelles of ionic surfactant in an aqueous solution bind ions on the surface of oppositely charged micelles via electrostatic interactions. To form ionic surfactant micelles, the amount of anionic surfactant should be greater than its critical micellar concentration (CMC). Lowering the CMC of anionic surfactant by adding nonionic surfactant has been demonstrated and applied in MEUF process for treating metal ions (Juang *et al.,* 2003).

The objective of this study is to discuss and compare the retention characteristics of Manganese in presence of Sodium Dodecyl Sulfate (SDS), anionic surfactant by MEUF. The influences of feed flow rate, operating time, surfactant/metal (S/M) ratio, feed pH and feed Mn^{2+} concentration on rejection efficiency of Mn^{2+} were studied.

II. Experimental

2.1 Materials

Manganese (II) sulfate monohydrate ($MnSO_4$. H_2O) was used as source of metal ion supplied by Merck Ltd., Mumbai, India. The surfactant, Sodium Dodecyl Sulfate (SDS) was used without any further purification received from Merck Ltd., Mumbai- India. 0.5 N H_2SO_4 and 0.5 N NaOH, were used for adjusting pH of solution obtained from SD Fine Chemicals, Mumbai- India. Cetylpyridinium chloride (CPC), chloroform, methylene blue indicator used for SDS analysis, 4-(2-pyridylazo) resorcinol monosodium salt (PAR) used for Mn^{2+} analysis were procured from SD Fine Chemicals, Mumbai-India.

Deionized water was used in all the experimental run. All the chemicals were of analytical grade and with ≥98.5% purity.

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The polysulfone (PS) membrane with 10kDa MWCO and effective area 200 cm^2 for ultrafiltration cell was procured from Sartorious (Germany).

2.2 Experimental Setup

A cross flow continuous mode system, from Sartorious, Germany, was used to carry ultrafiltration experiments. The feed solution containing the mixture of aqueous metal solution and surfactant was placed in feed tank of 400 ml of capacity. A peristaltic pump was used to feed the solution to ultrafiltration cell in which the membrane was sandwiched between the stainless steel flanges. The ultrafiltration cell contains input for feed and two output as permeate and retentate in which each having pressure sensors. The permeate and retentate were recycled back to the feed tank to maintain the system in continuous mode. Amount of samples were collected at a particular run time from the respective valve. After each run, membrane was cleaned by back flushing with DI water.

2.3 Experimental Procedure

Laboratory wastewater was prepared by dissolving Manganese (II) sulfate monohydrate ($MnSO_4$. H_2O) in DI water. $MnSO_4$. H_2O and surfactant in the desired ratio dissolved in DI water was prepared as a feed solution. For every run, 400ml of water was taken as feed volume and the process was carried out at room temperature (29±2^{0}C).

Before and after each run, permeate flux was calculated using DI water to check permeability of membrane. After each run, the membrane was cleaned with DI water by using back flushing for 30 minutes. pH of the solution was adjusted by addition of 0.5 N NaOH and 0.5 N H_2SO_4. Amount of sample was collected at particular time for further analysis and permeate flow rate was also calculated.

2.4 Analytical methods

Manganese analysis: UV/VIS Spectrophotometer was used to analyze the unknown Mn2+ concentration by standard curve. The maximum absorbance was measured at 504 nm on the addition 4-(2-pyridylazo) resorcinol monosodium salt (PAR) indicator.

Sodium Dodecyl Sulphate(SDS) analysis: Two phase titration method was used to analyze the unknown SDS concentration, titrating with known concentration of Cetylpyridinium Chloride (CPC) using methylene blue indicator and chloroform.

The retentate concentrations were calculated using material balance as follows;

$$C_F V_F = C_P V_P + C_R V_R$$

$$C_R = \frac{C_F V_F - C_P V_P}{V_R}$$

Where, C_F, C_P, C_R are concentrations of Mn^{2+} in feed, permeate and retentate and V_F, V_P, V_R are volume of feed, permeate and retentate.

Rejection analysis:

$$\%R_{Mn^{2+}} = \left[1 - \left(C_{P_{Mn^{2+}}}\right)/\left(C_{F_{Mn^{2+}}}\right)\right] \text{ x } 100 \quad (1)$$

$$\%R_{SDS} = \left[1 - \left(C_{P_{SDS}}\right)/\left(C_{F_{SDS}}\right)\right] \text{ x } 100 \quad (2)$$

The subscript P and F indicates corresponding quality as measured in permeate and feed respectively.

III. Results And Discussion

3.1Ultrafiltration of Mn^{2+} without surfactant

400 ml of 1mM feed solution was prepared by dissolving Manganese Sulphate Monohydrate in DI water. By this study, 39% Mn^{2+} was removed from 1mM concentration without surfactant which was almost considered as half of the feed concentration shown in fig.2. Thus, there is no adsorption of metal ions on the membrane resistance is almost zero (Karate and Marathe, 2008). The rejection efficiency without surfactant attributed to hydrophobic membrane and hydrophilic solute interaction offering some membrane resistance (Kamble and Marathe, 2005 and Chhatre and Marathe, 2006).

3.2 Optimization of flow rate

400ml of feed solution was prepared by dissolving Manganese Sulphate Monohydrate with SDS with S/M ratio 5 and pH 7.6. The feed flow rate varied as 50 to 175ml/min with the difference of 25 ml/min. Before each run membrane was back flushed with DI water.

From fig. 3, the maximum rejection efficiency of Mn^{2+} was obtained at 125 ml/min. This flow rate was used as standard for all the rest of the experiments. Rejection efficiency of Mn^{2+} increased with feed flow rate since increase in feed flow rate results in increase of feed pressure which directly affects the micelles, letting it to pass through the membrane pores or reject it. Hence, it was observed that at lower feed flow rate (< 125 ml/min), micelles easily pass through the membrane as there is no pressure and at higher feed flow rate (> 125 ml/min), more pressure was experienced on micelles to get forcibly pumped through membrane pores along with the monomeric surfactant and unbound metal ions(Karate and Marathe, 2008).

3.3 Effect of time

Feed passing through the membrane was having S/M =5, pH=7.6. The samples were collected from 10 to 100 minutes with the interval of 10 min. In fig. 4, it was observed that after 60th min, the equilibrium was attained and maximum rejection was obtained. This trend may be explained as in terms of concentration polarization, namely SDS micelle deposit on the membrane surface (Liu and Li, 2005).

3.4 Effect of surfactant to metal ratio (S/M)

On changing the concentration of SDS while Mn^{2+} concentration was kept constant, the S/M ratio was varied from 5 to 8. The Maximum rejection efficiency was obtained from S/M ratio 7 shown in fig. 5. This may be attributed to the fact that at 8 mM which is CMC of SDS, expected to give maximum rejection (Liu and Li, 2005). But, in this case while addition of 1 mM Mn^{2+}, the CMC of SDS decreases to 7 mM from 8 mM at which the maximum rejection was obtained as shown in fig.6

3.5 Effect of pH

On addition of 0.5N NaOH and 0.5N HCl, the feed solution with different pH varying from 3 to 10 were prepared. The samples were collected after 60th min for further analysis. The maximum % rejection was obtained at pH value 8 and after that it varied consistently, shown in fig.7. So it is evident that at low pH there are a lot of protons in the solution and it makes functional group protonated (Ahmadi et al., 1995 and Lin, 2003). On the contrary at higher pH, H^+ ions bound with functional groups can be dissociated easily and deprotonated functional group can bind with Mn^{2+} ions.

3.6 Effect of feed Mn^{2+} concentration

On keeping S/M ratio constant at 7, and the concentration of Mn^{2+} varied from 0.5 mM to 3 mM. as shown in fig. 8, it was observed that as concentration of Mn^{2+} increases in feed, % rejection efficiency of Mn^{2+} decreases. At much lower concentration of 0.5 mM Mn^{2+}, % rejection was observed to be very less as the concentration of surfactant used was below CMC (3 mM) of SDS, thus the micellization is not effective. At very high concentration, the drop in rejection may be attributed to either the lack of availability of binding sites or the micellar shape changes from spherical to cylindrical or plate like and thus these can be easily passed through the membrane pores resulting in considerable drop in rejection of metal ions (Karate and Marathe, 2008).

3.7 Performance of MEUF

The micelle loading (Lm), micellar binding constant (Kp) and the distribution coefficient (D) were calculated to understand the performance of MEUF. Micelles of surfactant are in equilibrium with individual surfactant molecules, passing through the pores of a membrane and are dynamic aggregates. The characteristics of an exchange of one surfactant molecule between micelle and the bulk, and the micelle breakdown are function of residence time and micelle lifetime.

These values can be calculated by using the following equations;

$$\text{Distribution coefficient (D)} = \frac{[M]_R}{[M]_P} \tag{3}$$

$$\text{Micellar Loading (Lm)} = \frac{[M]_R - [M]_P}{[S]_R - CMC} \tag{4}$$

$$\text{Micellar binding constant (Kp)} = \frac{[M]_M}{[M]_W \times [S]}\ \text{mol}^{-1} \tag{5}$$

Where, subscripts R, P indicate retentate and permeate stream and [M], [S] indicate concentration of metal ion and surfactant, respectively.

$[M] = [M]_R - [M]_P$

$[M]_w = [M]_P$

$[S] = [S]_R - CMC$

Fig. 9 and 10 explain the effect of metal ions and surfactant concentaration in the feed on distribution coefficient, micellar loading and micellar binding constant. As surfactant concentration increases, the rejection efficiency of Mn^{2+} and SDS increases which was represented by above equations. An increase in the value of D indicates that more and more surfactant molecules join the micellar phase, binding more and more metal ions (Karate and Marathe, 2008).

IV. CONCLUSIONS

MEUF is an effective method for removal of Manganese (Mn^{2+}) ions from wastewater using SDS surfactant.

Maximum rejection efficiency (> 97%) can be obtained by optimizing the parameters like feed flow rate at 150 ml/min, S/M ratio 7, pH 8 and feed concentration of Mn^{2+} 1 mM.

The micelle loading, micellar binding constant and distribution coefficient can be estimated to confirm the reproducibility of the results.

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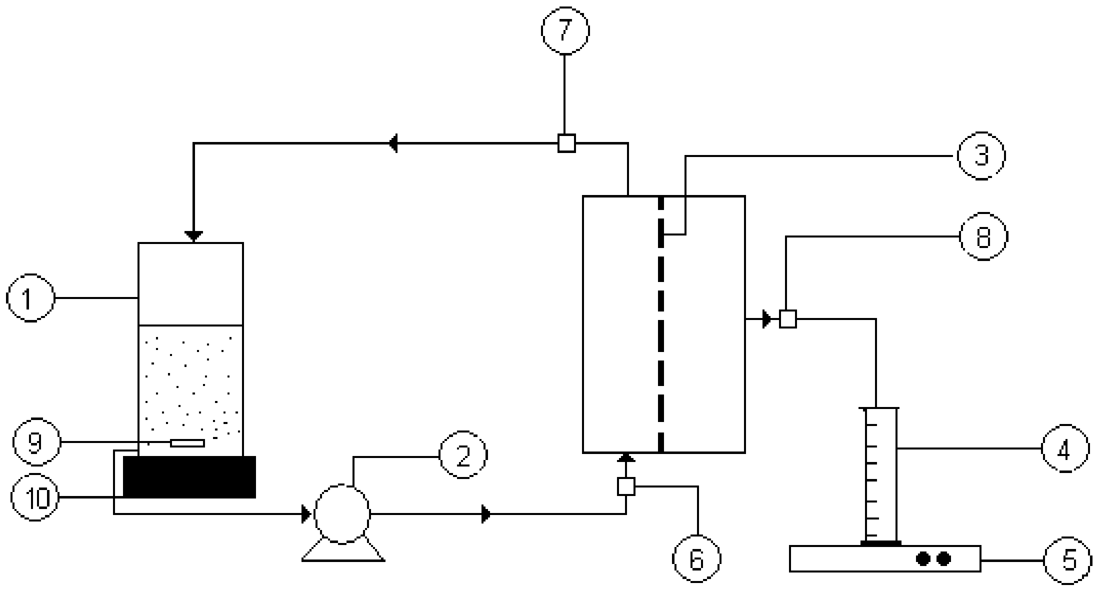

Fig.1. Schematic representation of cross flow ultrafiltration: Feed tank; 2.Peristaltic pump; 3.Polysulfone membrane; 4. Measuring cylinder; 5.weigh balance; 6. Feed inlet pressure sensor; 7. Permeate pressure sensor; 8. Retenate pressure sensor; 9. Magnetic stirrer; 10. Magnetic motor

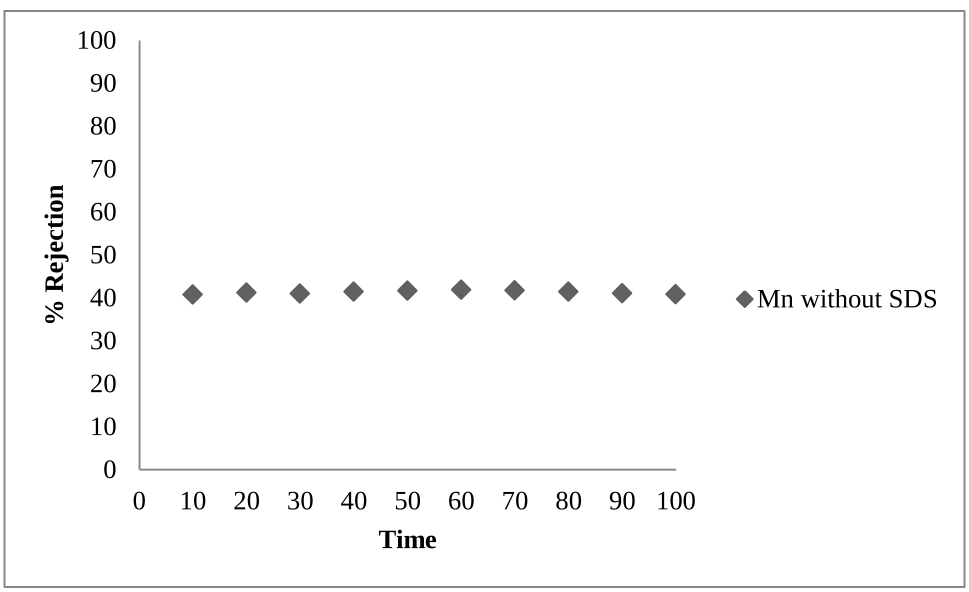

Fig. 2. Ultrafiltration of Mn^{2+} without surfactant

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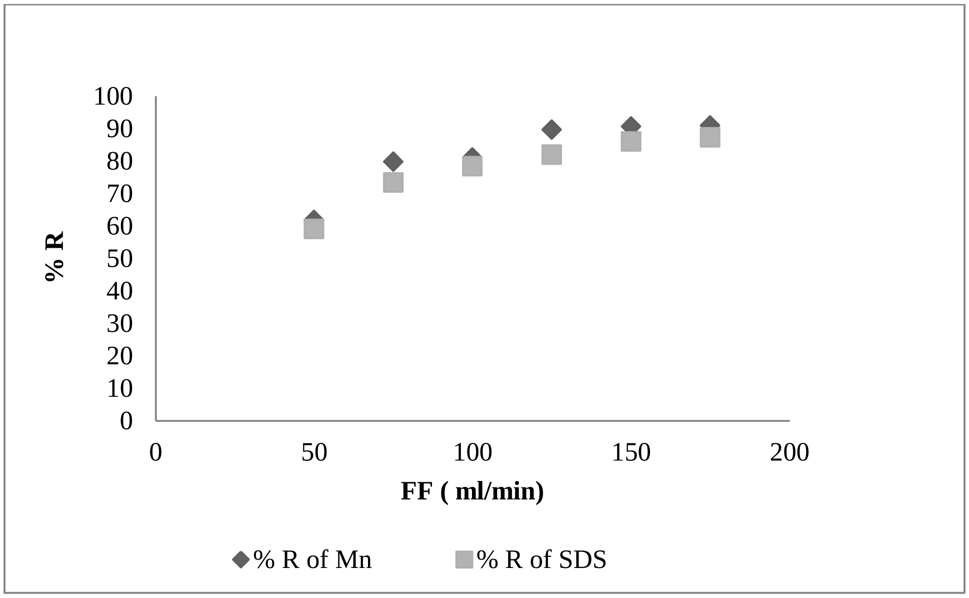

Fig. 3. Effect of feed flow rate on % rejection of Mn and SDS

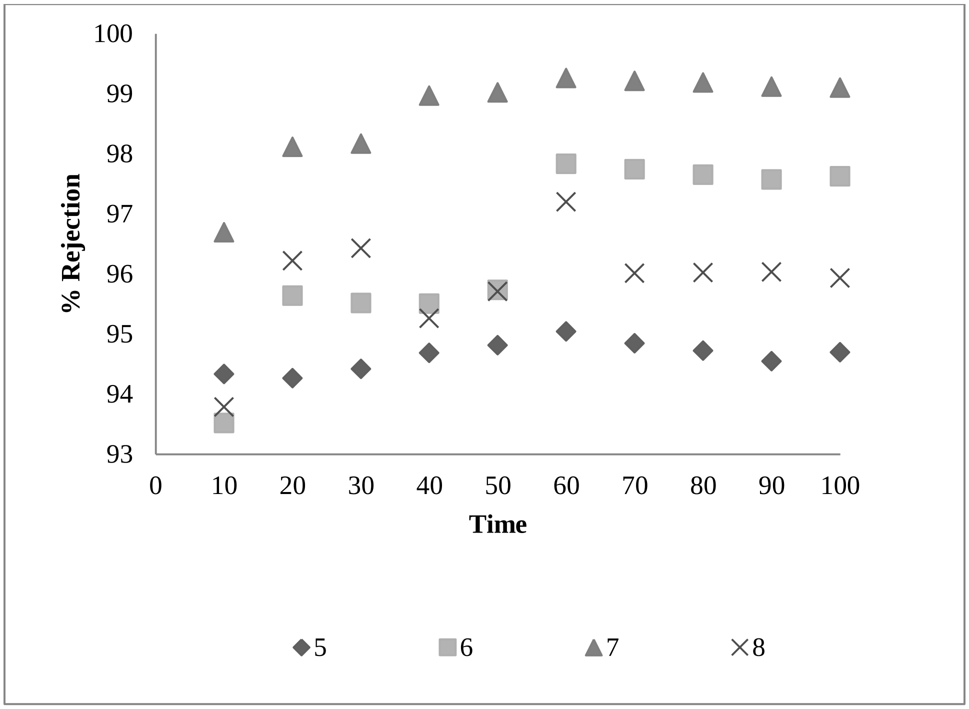

Fig. 4- Effect of time on % rejection of Mn varying S/M ratio

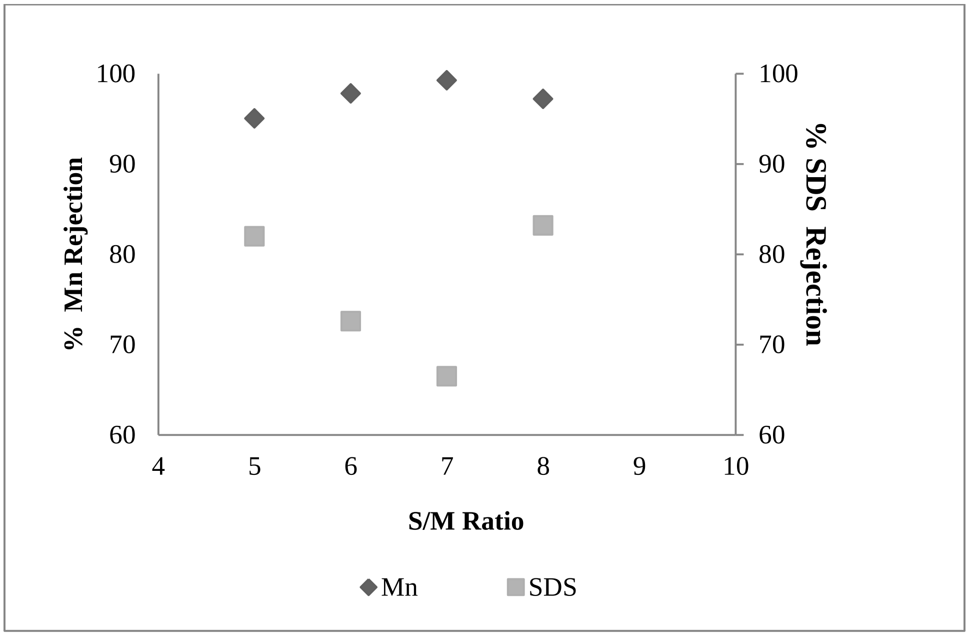

Fig. 5. Effect of surfactant to metal ratio on % rejection of Mn and SDS

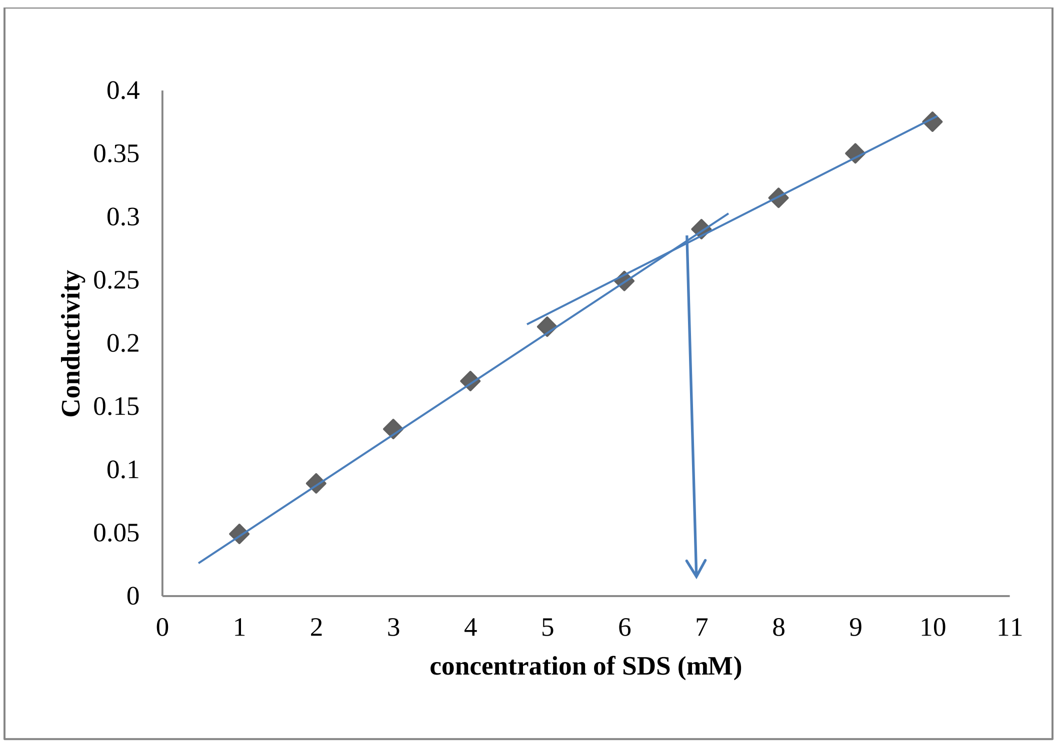

Fig. 6 Effect of 1mM Manganese on CMC of SDS

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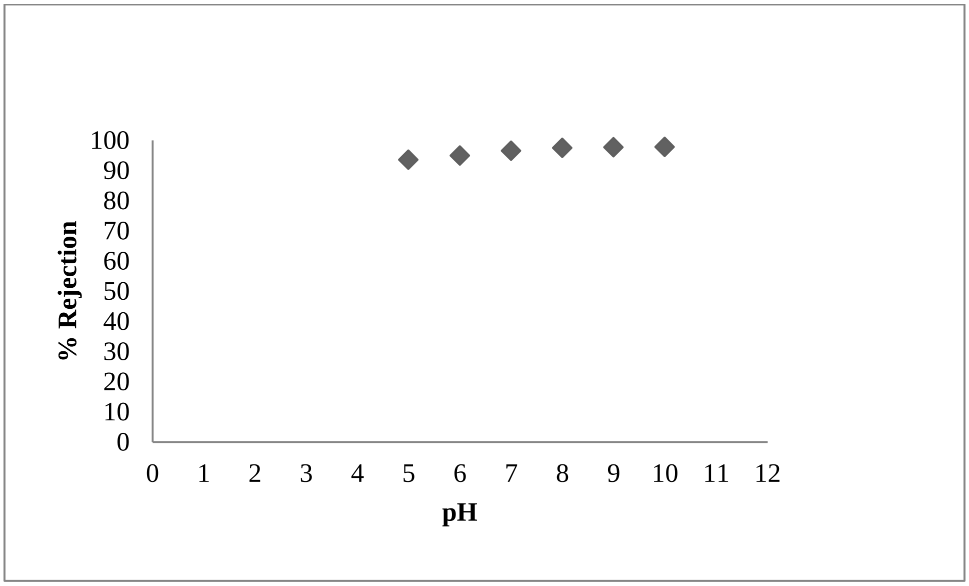

Fig. 7 Effect of pH on % rejection Mn

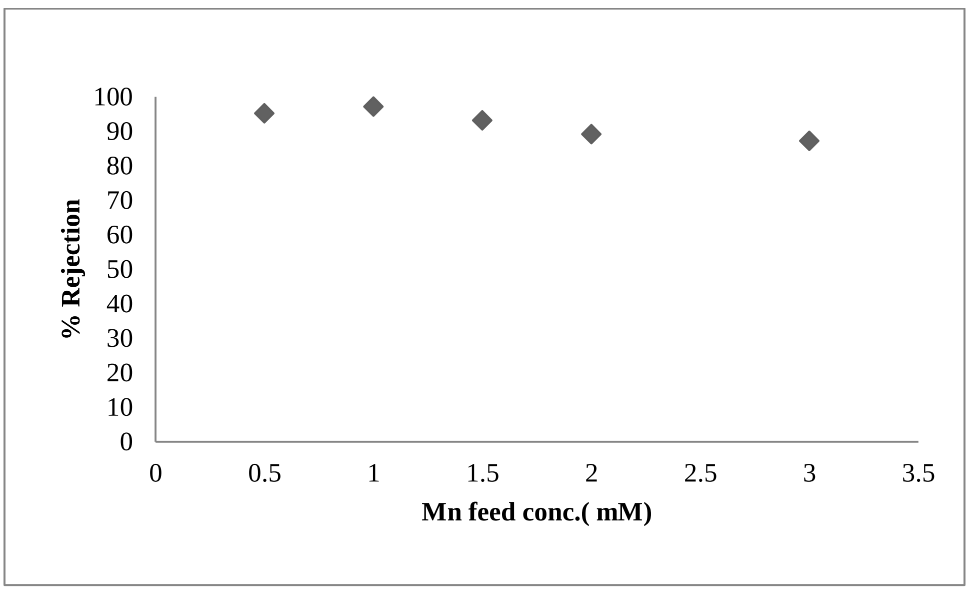

Fig. 8 Effect of Feed Mn^{2+} concentration on % rejection of Mn

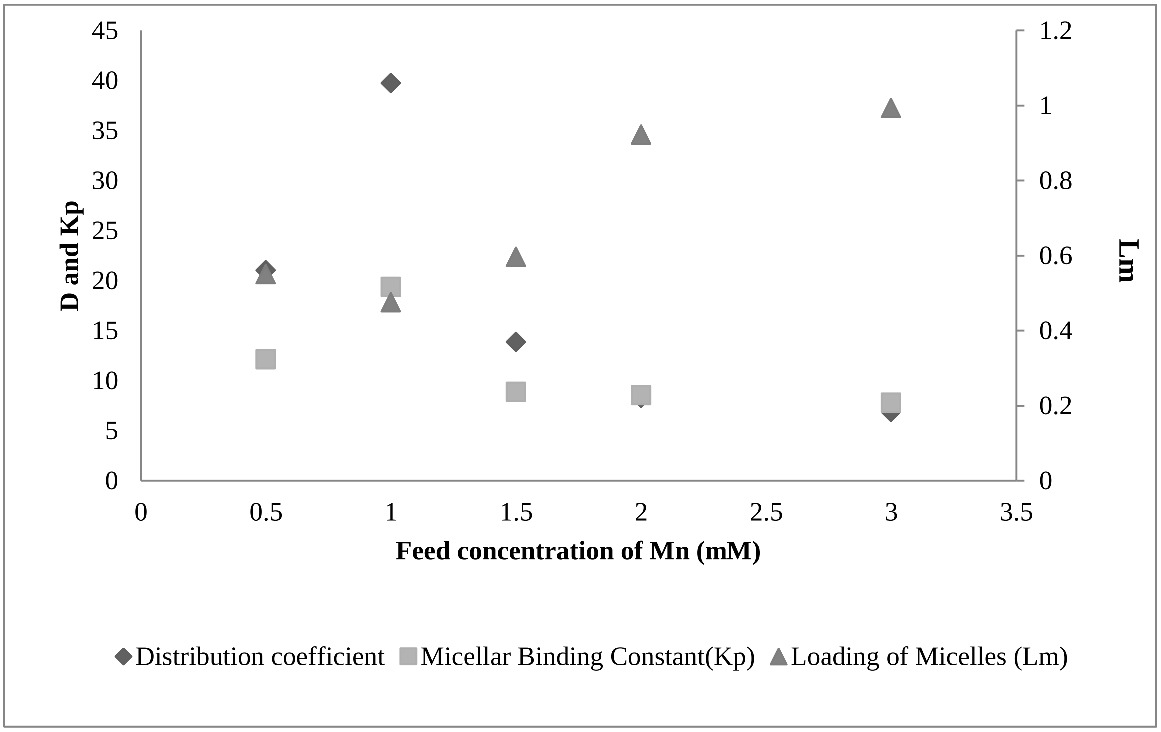

Fig.9 Effect of feed concentration of Mn on D, Kp and Lm

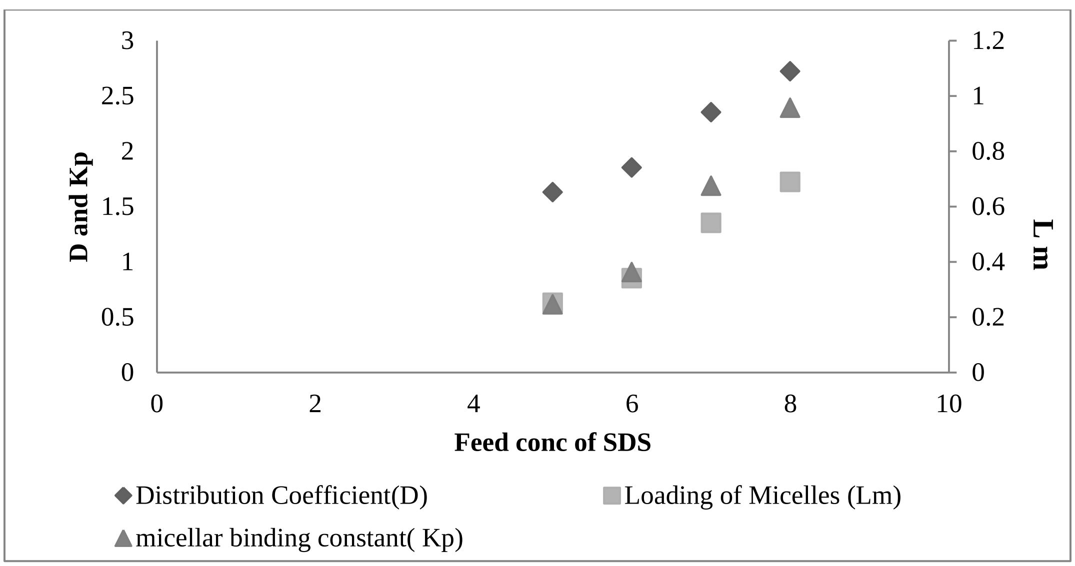

Fig. 10 Effect of feed concentration of SDS on D, Kp and Lm