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Removal of Pb (II) from Waste Water by Using Synthesized Iron and Iron Alloy Nanowires

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Nanowires of iron, iron-nickel and iron-cobalt alloy were synthesized from aqueous solution of iron sulphate, nickel sulphate and cobalt sulphate by template assisted electrodeposition method using anodized aluminium oxide as template. Morphology of nanoporous anodized aluminium oxide (AAO) and nanowires were confirmed with FE-SEM and EDS analysis. FE-SEM analysis shows that deposited nanowires were parallel to each other and have high aspect ratio with a reasonably high pore filling factor. The electrodeposited nanowires have varying length, approximately 650 nm for iron , 684nm for iron-nickel and 964nm for iron-cobalt nanowires after optimizing various parameters involved. Further, comparative study of removal of Pb (II) from effluent was done using these fabricated nanowires and it was found that iron-cobalt nanowires having more length show maximum adsorption of Pb (II) as compared to iron nanowires and iron-nickel nanowires.

Keywords: Anodized Aluminum oxide (AAO), Electrodeposition, Nanowires, Iron-cobalt alloy.

1. Introduction

Rapid growth in nanotechnology and nanosciences occurred in the last decades due to novel tools and routes available for the fabrication of nanostructures. Out of many nanostructures available, tubular and elongated ones have attracted a lot of interest due to their unique physical and chemical properties, which are interesting from the view point of different device applications (1-4). Synthesis and processing of nanowires is essential aspect of nanotechnology. Metallic nanowires and their alloys are widely used nanostructures because of their applications in magnetic, electronic, sensor elements and in biological fields(5-7). Out of various formal techniques used for fabrication of nanowires, electrodeposition via template assisted method is preferred as it is environmental friendly , has high growth rate at room temperature, cost effective and has easy control of shape and size. In literature, most of the researchers have used anodic aluminium oxide as template which can withstand high temperatures, is insoluble in organic solvents and their geometrical parameters can be easily tuned by changing the synthesis conditions (8-11). Moreover, mass production of nanowires can be achieved with controlled morphology and geometry if some parameters are controlled during synthesis of template, which further can have various environmental applications (12-13).

Recently, many researchers have fabricated metal and metal oxide nanowires by using different methods and have explored their wide applications but negligible work has been reported in literature to explore environmental applications of metallic nanowires fabricated via electrodeposition method. Presence of heavy metals in waste water poses serious threat to the human health, so their removal from water is of great concern these days. High purity nanowires with high aspect ratio can be promising adsorbents for their removal (14-16). Thus the aim of our present work is to fabricate high purity iron, iron-nickel, iron-cobalt nanowires of desirable length by controlling various parameters involved during anodization and electrochemical deposition in templates. Further, comparative study of these fabricated nanowires in removal of carcinogenic Pb (II) from the effluent has been done to explore maximum removal through the process of adsorption.

2. Experimental

2.1. Preparation of Anodic Aluminium Oxide (AAO)

Specimens of aluminium were punched from 0.4mm thick, 99.99% pure sheet, having dimensions 10 cm × 2 cm. After cutting, samples were first degreased in ethanol for 3 minutes, washed in deionized water and air dried. Then, specimen was coated with lacquer leaving the area of 1cm×1cm ,which is being used for template synthesis. After that electropolishing of samples was carried out using 1:5 mixture of perchloric acid and ethanol. The electropolishing time was varied from 1 minute to 6 minutes at 15 V having temperature ranges 30 ± 5 ^{0}C. This pretreatment is given to decrease surface roughness of samples so that best quality of anodized aluminium oxide layers must be obtained. The roughness of surface was tested with surface roughness tester. Electropolished samples were then anodized in an electrochemical bath using sample as anode and Al as cathode. Anodization was carried out in 0.3 M phosphoric acid solution (pH 1.1) at constant temperature 30 $\pm$ 5 ^{o}C with varying potential range from 120 V to 160 V for 1hr. To get more ordered pores thinning of barrier layer is done by using 100 ml solution made by mixing 1.8% of H_2CrO_4 and 6% of H3PO4 at 70◦C for 1 hr. After thinning of barrier layer, samples were air dried and again anodized as in one step. To widen the pores, the samples were dipped into 3% (by wt) orthophosphoric acid solution for 20 minutes.

2.2. Fabrication of Nanowires by Electrodeposition

Electrodeposition of iron nanowires into nanopores was carried out by using mixture of 20g of Ferrous sulphate, 0.5g of Ascorbic acid and 3g of Boric acid at AC voltage of 15V for 2-5 minutes. Two anodized samples were dipped simultaneously in electrodeposition mixture. For iron-nickel nanowires, equimolar mixture of Ferrous sulphate and Nickel sulphate was used.For iron-cobalt nanowires, mixture of Ferrous sulphate and Cobalt sulphate was used in the ratio of 1:1. Boric acid (1.5g/L) was added in each bath so that deposition was facilitated and hydroxide formation was avoided. During deposition, solution was constantly stirred. Deposition time was 2-5 minutes at 15V.After co-electrodeposition process, samples were washed with deionized water and dried. Electrodeposited samples were kept in 1M NaOH for alumina dissolution for 10 minutes, whereas the nanowires remain stable in the porous AAO template. FE-SEM of these nanowires was taken to study their parameters like diameter and length etc.

2.3. Adsorption Study

Synthesized Iron, Iron-Nickel and Iron-Cobalt nanowires were used for adsorption of Pb (II) from waste water separately. For adsorption, stock solution was prepared by dissolving 1.6 g of Pb $(NO_3)_2$ in 1lt of deionized water. The pH of solution was adjusted to 6 by adding a few drops of HCl. Fabricated nanowires were immersed in 50 ml of Pb (II) solution at room temperature separately. UV-Visible spectrophotometer was used to study adsorption at 540 nm after 15 minutes intervals.

3. Results and Discussion

AAO needed for the fabrication of nanowires was synthesized by anodizing electropolished samples in 0.3 M H_3PO_4 at 150 V and 30 ± 5 ^{0}C for 1 hr. Electropolishing of the specimen was done with 1:5 mixture of perchloric acid and ethanol for 3 minutes at which maximum smoothness of the surface was observed i.e. with surface roughness value 0.188µm. FE-SEM images corresponding to different parameters are shown in Figure 1.

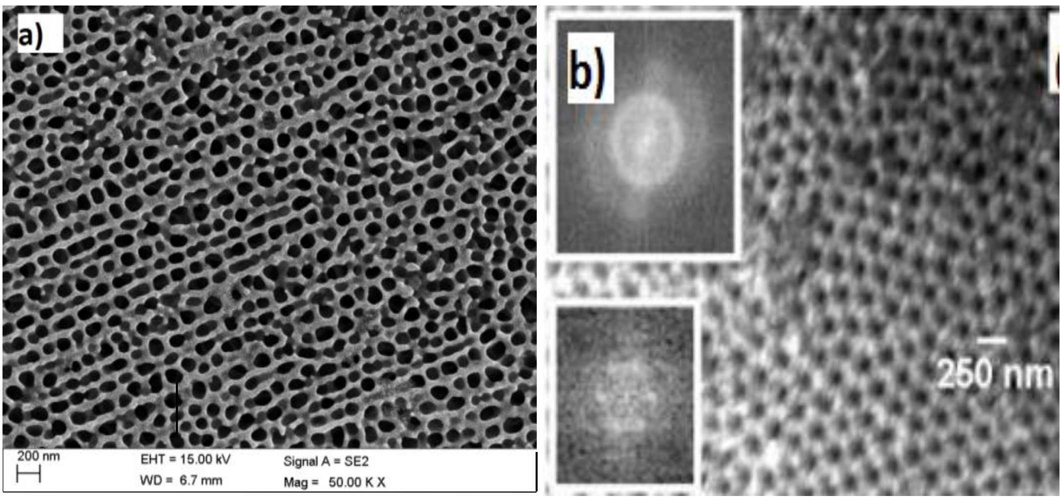

Figure 1. FE-SEM top view micrographs for anodized samples at 150 V in 0.3 M H_3P0_4 for 1 hr at 30 ± 5 ^{0}C at a scale of a) 200 nm b) 250 nm with FFT showing regularity of pores.

Electrodeposition was carried out at a.c. by having mixture of Ferrous Sulphate, Boric acid and Ascorbic acid for iron nanowires, 1:1 mixture of Ferrous Sulphate- Nickel Sulphate for iron-nickel nanowires and 1:1 mixture of Ferrous sulphate-Cobalt Sulphate for iron cobalt nanowires. To get the cross sectional view of synthesized nanowires, template was cut from the middle. Nanowires of iron, iron-nickel and iron-cobalt as synthesized by electrodeposition are shown in Figure 2.

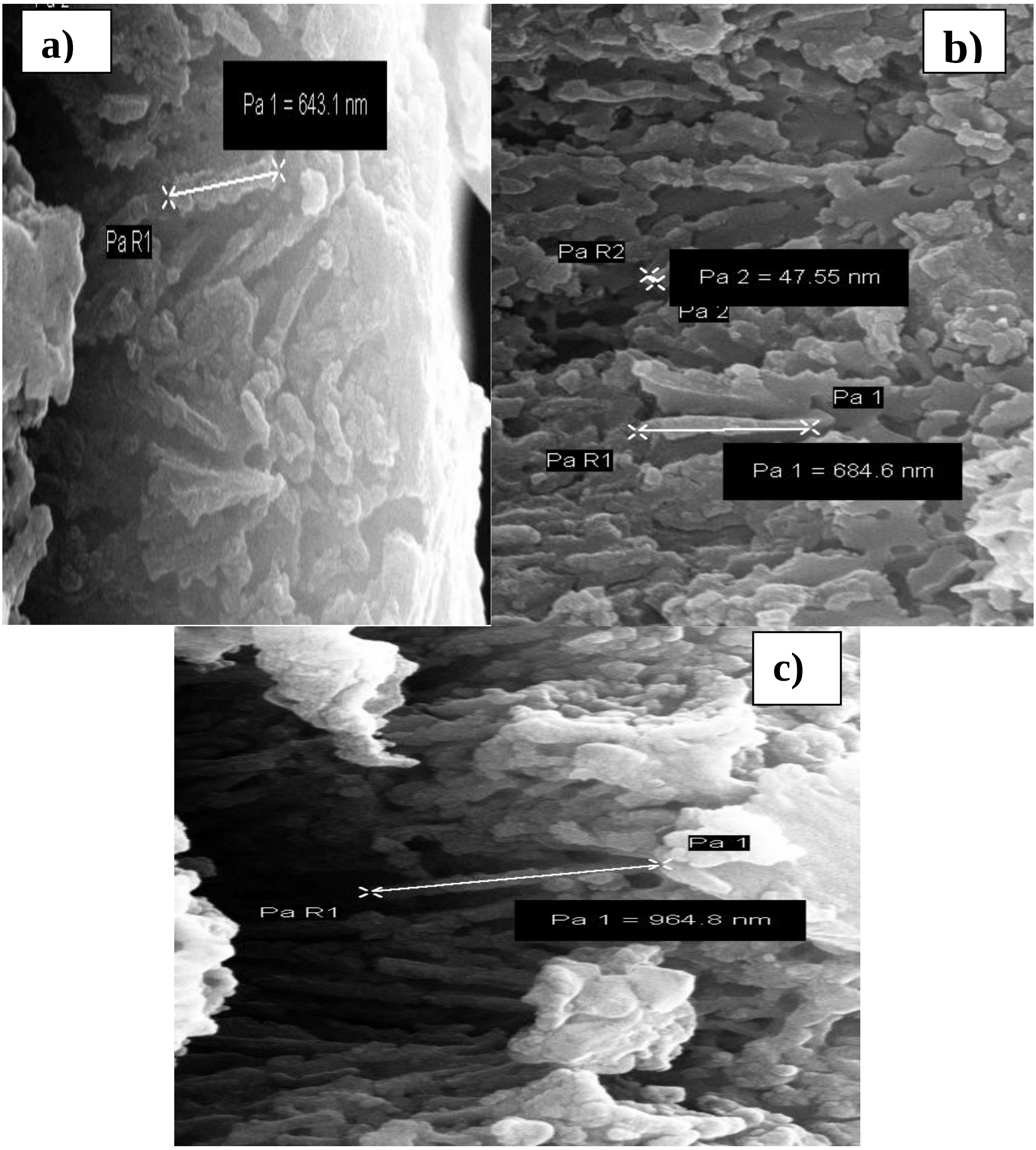

Figure 2. FE-SEM cross-sectional view micrographs of nanowires anodized at 150 V in 0.3 M H_3P0_4 for 1 hr at 30 ^{0}C a) Iron Nanowires b) Iron-Nickel Nanowires c)Iron-Cobalt Nanowires

In Figure 2, rod shaped nanowires of iron, iron-nickel and iron-cobalt are shown having length of 643 nm,684nm and 964nm respectively with a diameter of 103.0 nm. Confirmation of nanowires was done by EDX compiled with FE-SEM as shown in Figure 3.

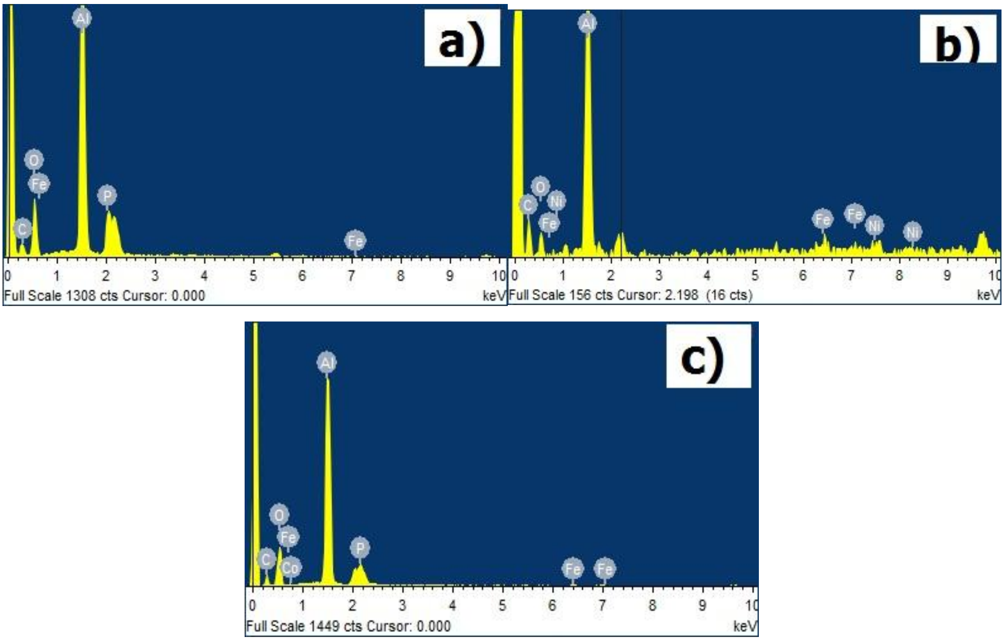

Figure 3. EDS confirmed the iron,iron-nickel and iron-cobalt nanowires in nanoporous anodic alumina by electrodeposition.

Table 1 shows the percentage removal of Pb (II) with iron nanowires, Table 2 shows Pb (II) removal with iron-nickel nanowires and Table 3 shows with iron-cobalt nanowires. As shown in tables, adsorption first increases with time and then attained a constant value when adsorption equilibrium had been established. The main reason behind the adsorption is electrostatic forces of attraction between nanowires having positive charge and Pb (II) carrying negative charge at pH 6.

Table 1. Percentage Removal of Pb (II) from Waste Water by using Iron Nanowires

S.no.	Conc. (mg/l)			Time (In minutes)	% age removal $\frac{(C_0 - C_e)}{C_0} \times 100$
	C_0	C_e	X		
1.	0.021	0.015	0.006	15	28.57
2.	0.021	0.014	0.007	30	33.33
3.	0.021	0.011	0.010	45	47.62
4.	0.021	0.010	0.011	60	52.38
5.	0.021	0.009	0.012	75	57.14
6.	0.021	0.009	0.012	90	57.14

Table 2. Percentage Removal of Pb (II) from Waste Water by using Iron-Nickel Nanowires

S.no.	Conc. (mg/l)			Time (In minutes)	% age removal $\frac{(C_0 - C_e)}{C_0} \times 100$
	C_0	C_e	X		
1.	0.021	0.014	0.007	15	33.33
2.	0.021	0.013	0.008	30	38.10
3.	0.021	0.012	0.009	45	42.86
4.	0.021	0.009	0.012	60	57.14
5.	0.021	0.007	0.014	75	66.67

6.	0.021	0.007	0.014	90	66.67

Table 3. Percentage Removal of Pb (II) from Waste Water by using Iron-Cobalt Nanowires

S.no.	Conc. (mg/l)			Time (In minutes)	% age removal $\frac{(C_0 - C_e)}{C_0} \times 100$
	C_0	C_e	X		
1.	0.021	0.013	0.008	15	38.10
2.	0.021	0.012	0.009	30	42.86
3.	0.021	0.011	0.010	45	47.62
4.	0.021	0.009	0.012	60	57.14
5.	0.021	0.005	0.016	75	76.19
6.	0.021	0.005	0.016	90	76.19

The adsorption in case of iron-cobalt wires is more as compared to iron-nickel and iron nanowires due to enhancement in length of nanowires. As length of nanowires increases their adsorption capacity also increases due to more available adsorption sites. Figure 4 shows graphs indicating percentage removal of Pb (II) with time.

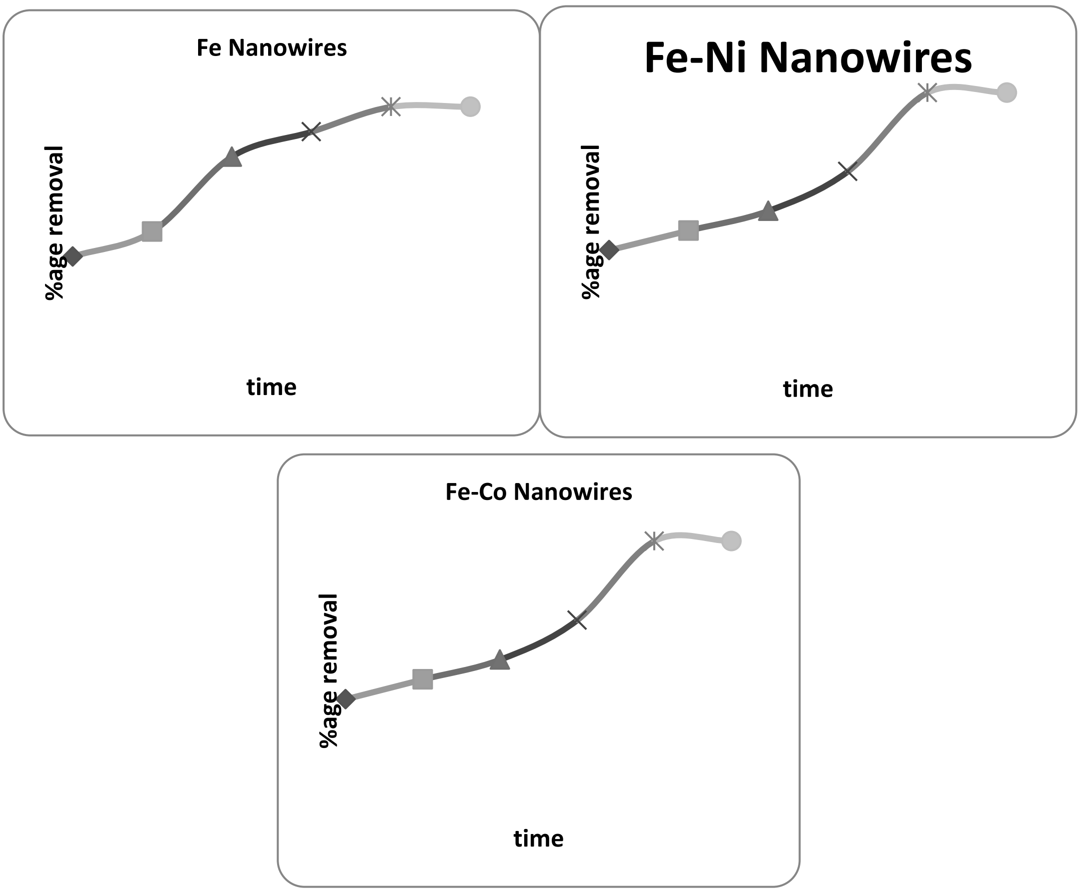

Figure 4. Graphs showing percentage removal of Pb (II) at time intervals

The most widely used isotherms equation for modelling of the adsorption data i.e. Langmuir isotherm has also been plotted for adsorption studies.Experimental results obtained for the removal of Pb (II) w.r.t. synthesized nanowires (act as adsorbent) on porous AAO adsorbent were found to be best fitted to Langmuir isotherm model.Tables 4,5 and 6 shows the adsorption characterstics . The plot between Ce/X and Ce yield straight line indicating that the synthesized nanowires are promising candidate for the removal of hazardous Pb (II). The Langmuir adsorption isotherm is presented in Figure 5.

Table 4. Adsorption Characteristics (Langmuir) of Pb (II) by Fe Nanowires.

	Conc.(mg/l)			
S.No.	C_0	C_e	X	C_e /X
1	0.021	0.015	0.006	2.500
2	0.021	0.014	0.007	2.000
3	0.021	0.011	0.010	1.100
4	0.021	0.010	0.011	0.909
5	0.021	0.009	0.012	0.750
6	0.021	0.009	0.012	0.750

Table 5. Adsorption Characteristics (Langmuir) of Pb (II) by Fe-Ni Nanowires

	Conc.(mg/l)			
S.No.	C_0	C_e	X	C_e /X
1	0.021	0.014	0.007	2.000
2	0.021	0.013	0.008	1.600
3	0.021	0.012	0.009	1.330
4	0.021	0.009	0.012	0.750
5	0.021	0.007	0.014	0.500
6	0.021	0.007	0.014	0.500

Table 6. Adsorption Characteristics (Langmuir) of Pb (II) by Fe-Co Nanowires.

	Conc.(mg/l)			
S.No.	C_0	C_e	X	C_e /X
1	0.021	0.013	0.008	1.600
2	0.021	0.012	0.009	1.300
3	0.021	0.011	0.010	1.100
4	0.021	0.009	0.012	0.750
5	0.021	0.005	0.016	0.313
6	0.021	0.005	0.016	0.313

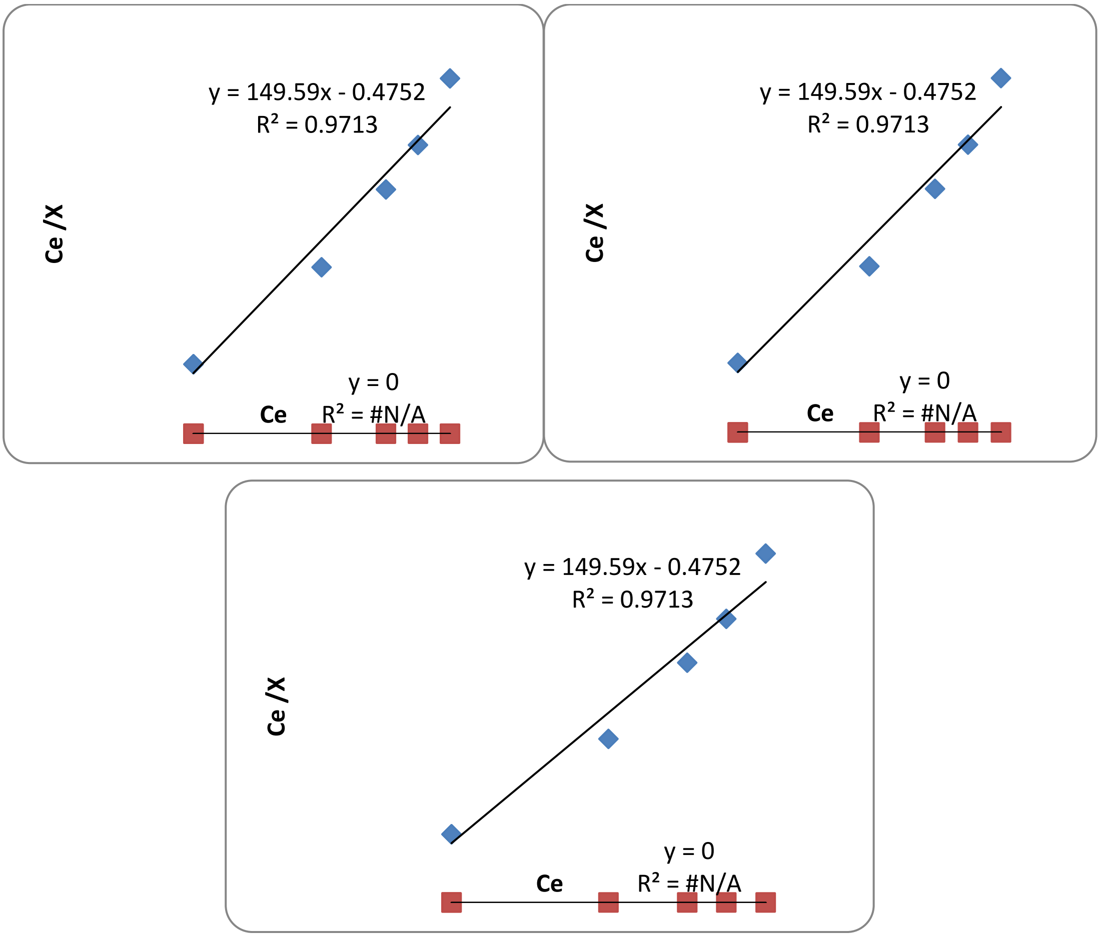

Figure 5. Langmuir Isotherm between Ce/X and Ce

4. Conclusion

In the present paper, synthesis of iron ,iron-nickel and iron-cobalt nanowires via electrodeposition process has been reported and their potential environmental application has been explored by the removal of Pb (II) from the waste water. The results of FE-SEM with EDX confirmed the composition of fabricated nanowires is of iron, iron –nickel and iron - cobalt alloy. On comparison of removal efficiency of iron,iron-nickel and iron-cobalt nanowires to remove Pb (II) from waste water , it has been found that the %age removal of Pb (II) by using iron nanowires was minimum i.e.57.14% and maximum by using iron-cobalt nanowires i.e.76.19% from the industrial waste water. So iron-cobalt nanowires are found to be most promising adsorbent for the removal of Pb (II) from the effluent.

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