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Selective Co (II) Removal from Aqueous Media by Immobilizing the Silver Nanoparticles within a Polymer-Matrix through Formaldehyde Cross Linking Agent

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Abstract:

Silver nanoparticles (AgNPs) were synthesized by a biological reduction method using Cyperus rotundus grass extract (CRGE) and these were found to contain a regular diameter of 1-100 nm. The Polymer nanocomposites (PFR-AgNPs) were then built-up by encapsulating green synthesized AgNPs within a phenol-formaldehyde resin (PFR) as a cross linking agent using polycondensation method and applied to sorption of Co (II) from aqueous solution in a batch adsorption system as an initial concentration (30–150 mg/L), contact time (10–50 min) and temperatures (303–333 K). The non-diffusible negatively charged sulphonic acid groups bound to PFR template should significantly develop penetration and preconcentration of the goal metal cations from aqueous solution to interior plane of the polymeric matrix as well as make constructive conditions for Co (II) removal by AgNPs particles. Then the column adsorption studies were carried out for the Co (II) retention in the presence of alkali and alkaline earth metals (Na^+, Ca^{2+} and Mg^{2+}). While compared to PFR, PFR-AgNPs demonstrated extremely penetrative cobalt removal from wastewaters in the subsistence of contending Ca^{2+}, Mg^{2+}, and Na^+ at a large amount than the target heavy metal. Pseudo first order reaction, pseudo second reaction and Weber–Morris intraparticle diffusion models were used to analyze the data. The adsorption equilibrium data was explored by the Freundlich and Langmuir adsorption isotherm models and the reaction was found to show a relationship well with a Freundlich adsorption model. Free PFR-AgNPs and Co^{2+} loaded PFR-AgNPs were characterized by the FT-IR spectra (FT-IR), Scanning electron microscope (SEM), energy-dispersive microanalysis (EDX), thermo gravimetric analysis (TGA), and differential thermal analysis (DTA). The regenerant used for regeneration of the cation-exchange resin was 5% (w/w) NaCl. The experimental results verified that PFR-AgNPs cation exchange resin can be applied efficiently for the removal of Co (II) from aqueous media.

Keywords: Polymer nanocomposites; phenol-formaldehyde resin; AgNPs; Co (II) removal; Potential Donnan membrane effect.

1. Introduction

In many developing countries, contamination of the water by heavy metals is a severe issue and then several fatalities every year were caused through waterborne diseases around the world. Then the water pollution through noxious heavy metals during the discharge of industrial waste is a universal environmental crisis. The existence of heavy metal in all water bodies has been creditworthy for numerous health problems with plants, animals, and human beings. Heavy metals such as cobalt, lead, mercury and cadmium are associated with these activities. Hence, the segregation of these metals from wastewater is essential. Pollution with cobalt is of significant concern since the metal has observed common use in mining, metallurgical, paints, pigment, and electronics [1]. Cobalt is also present in the wastewater of nuclear power plants. The permissible limits of cobalt in the supplying water and stock wastewater as per environmental bureau of investigation are 0.05 and 1.0 mg/L, correspondingly [2]. The cobalt toxicity to human beings may reason serious severe health issues like asthma, allergy, heart damage and failure, liver and thyroid damage, mutations and developing cancer during exposure to ionizing radiation.

Therefore, it is vital to take efficient protection to avoid water pollution by removal of cobalt from aqueous solution. A number of methods exist for the remove of cobalt from industrial wastewater containing adsorption, electro flotation, chemical precipitation, reverse osmosis and ion exchange. Ion exchange is effective method for the removal of heavy metals from industrial wastewater and polluted water using polymeric cation exchange resin [3]. However, simple polymeric cation exchange resins normally entrap heavy metals by nonspecific electrostatic interaction as well as show unsatisfactory specific adsorption affinity for the objective cations [4]. Therefore, they were unable to entrap the heavy metals to attain the standard limits as per world health organization in the existence of other competing ions (alkali and alkaline earth metals). Hence, it demands the build-up a novel specific ion exchangers for selective removal of hazardous metals from wastewater. Previously we have been exploited the AgNPs (zero valent metal) as specific adsorbents for heavy metals in wastewater and amended environmental quality [5]. Nonetheless, these nanoparticles are generally exhibit as fine or ultrafine particles [6] and cannot be utilized for direct apply in fixed-bed or any flow-through systems owing to the extreme pressure drop and meager mechanical strength. To beat the scientific problems, hybrid sorbents were subsequently built-up by impregnating these nanoparticles within the schematic significant porous materials like activated carbon [7] and porous polymer [8]. Among these, the porous polymer is predominantly selective due to their convenient pore space, good mechanical strength and also the potential Donnan membrane effect exerted by the immobilized negatively charged sulfonic acid groups bound to the macroporous cation exchanger result in preconcentration and penetration enhancement of heavy metal ions prior to their effective segregation by the impregnated nanoparticles [9]. Herein a novel hybrid cation exchange resin is developed by encapsulating AgNPs within a macroporous phenol-formaldehyde cation exchanger for the removal of cobalt from aqueous solution. In the present work, the AgNPs was synthesized by green method (biological reduction method) using CRGE as per literature [10].

2. Experimental

2.1. Materials

The plant material used in the current study was Cyperus rotundus (Korai grass) and these are freely available in Tamil Nadu, India. Phenol and formaldehyde used were Fischer reagents (India). LR grade of Conc. H_2SO_4 was used. The other chemicals and reagents were of chemically pure grade (AnalaR) procured from SD Fine Chemicals, India.

2.2. Methods

Phenol (10 mL) and Conc. H_2SO_4 (11.5 mL) were blended gradually with continuous stirring and cooling, heated to about 70 ^{O}C on a hot water bath for 6 h, cooled directly in the ice-cold water and set aside overnight [11]. 1 % and 0 % AgNPs was mixed to phenol sulphonic acid and these constitute samples labeled as PFR-AgNPs and PFR. This mixture was polymerized with formaldehyde (12.5 mL) at 70 ^{O}C and treated at this temperature for 3 h to yield a dark brown chunky mass. It was subsequently ground, cleaned with distilled water and finally with double distilled (DD) water to remove excess free acid, dried, sieved (250 – 300 µm) using Jayant sieves (India) and preserved for characterization [12].

2.3. Characterization of the samples

The presence of AgNPs in the PFR-AgNPs was confirmed by using a UV–Vis spectrophotometer (UV-1800 SHIMADZU spectrophotometer) at the wavelength of 300-800 nm. FT-IR (SHIMADZU MODEL FT-IR spectrometer) spectra was used to the study the before and after Co (II) adsorption on resins using the IR-grade KBr pellets in the ratio of 1:200 at the wave number ranging from 400 to 4000 cm^{-1}. The morphology of free and Co (II) loaded resins were studied by SEM (Vega3 Tescan SEM instrument). For studying the elemental constitute of free and Co (II) loaded of adsorbent, EDX (Bruker machine) was used. The thermal degradation of the free and Co (II) treated resins were found out using TGA and DTA analyzer (SII MODEL 6000 thermal analyzer).

2.4. Batch, Column adsorption and Thermodynamics studies

Batch adsorption experiments were carrying out by introducing a preferred amount of PFR and PFR-AgNPs resin in 250 mL glass bottles separately containing Co (II) solutions of various concentrations (30-150 mg/L). The mixtures were stirring at 200 rpm using a remi rotator water bath shaking machine at 303 K to attain the equilibrium. The agitation time was varied from 10 to 50 min in the succeeding periods like 10, 20, 30, 40 and 50 min at 303 K to find the equilibrium. The residual concentration of the Co (II) ions in the aqueous medium was determined by using standard titration techniques as per the literature [13]. The equilibrium adsorption capacity (q_e) of the adsorbents was estimated with the help of following equation:

$$\mathbf{q_e = (C_o\text{-}C_e) \times V / M \qquad \text{--------------} \ (1)}$$

Where q_e is the equilibrium adsorption capacity (mg g^{-1}), C_e is the concentration of metal ion (mg L^{-1}) at equilibrium, V is the volume of solution (L) and M is the weight (g) of adsorbent.

Column experiment was performed with a fixed-bed glass column with 2.0 cm internal diameter and 35 cm height and packed with 2 cm (3.5 g) of PFR and PFR-AgNPs were packed within two separate columns. The column bed volume is 6.28 cm^3. The flow circulation was improved by an addition of glass wool beads. Cobalt (II) ions solution (initial concentration=5 mg/L) and other competing ions were used as influent with high concentration than the target heavy metals and fed through the column at a constant flow rate of 5 mL/min in down-flow mode. The effluent solution was collected at various time intervals and evaluated for Co (II) content using EDTA titration techniques. Breakthrough curves were calculated by plotting volume of the influent against the proportion of Co (II) ions concentrations in the effluent throughout the column for the adsorption of Co (II) from aqueous solution.

Adsorption between Co^{2+} and adsorbent can be obtained by physisorption or chemisorption or ion-exchange. If the adsorption can be made by physisorption, since the loosely bound metal ions can be effortlessly desorbed with distilled water. Alternatively, if the adsorption process is maintained by chemisorption or ion exchange or combination of both, followed by desorption to be done effectively by strong mineral acid solution. Therefore, desorption study can endow with an evident idea regarding the mechanism of adsorption and is useful in regeneration of the adsorbent and recovery of the metals. Herein, the % of regeneration level of Ion Exchangers were studied by using the 5 % (w/w) NaCl as the eluting agent

$$\text{\% of Regeneration} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \text{ --------- } \mathbf{(2)}$$

The thermodynamic equilibrium constants ($\ln K_C$) of the ion exchange reaction between Co^{2+} and H^+ ions in the adsorbent were obtained using 40 ml of 150 ppm stock solution of Co^{2+} ions at 303 K, 313 K, 323 K and 333 K. Thermodynamic parameters (ΔG, ΔH, and ΔS) were calculated by using Van't Hoff isotherm, Van't Hoff and Gibbs Helmholtz equation.

3. Results and discussion

3.1. UV–Vis, FT-IR, SEM-EDX, TGA and DTA analysis:

Previous studies exposed that the spherical silver nanoparticles exhibit absorption bands about 400–440 nm in the UV-Visible spectrophotometer [14] and reveal the association of silver nanoparticles. UV–Visible spectra showed that the broad surface plasmon resonance nearly at 410 nm (Fig.1a) and these indicate the presence of silver particles within the

PFR-AgNPs. Then the schematic structure of the PFR-AgNPs was shown in Fig.1b, the sulfonate functional group and AgNPs have potential active sites for the withholding of Co (II) from aqueous media, which were found out and discussed with additional information's in the subsequent sections.

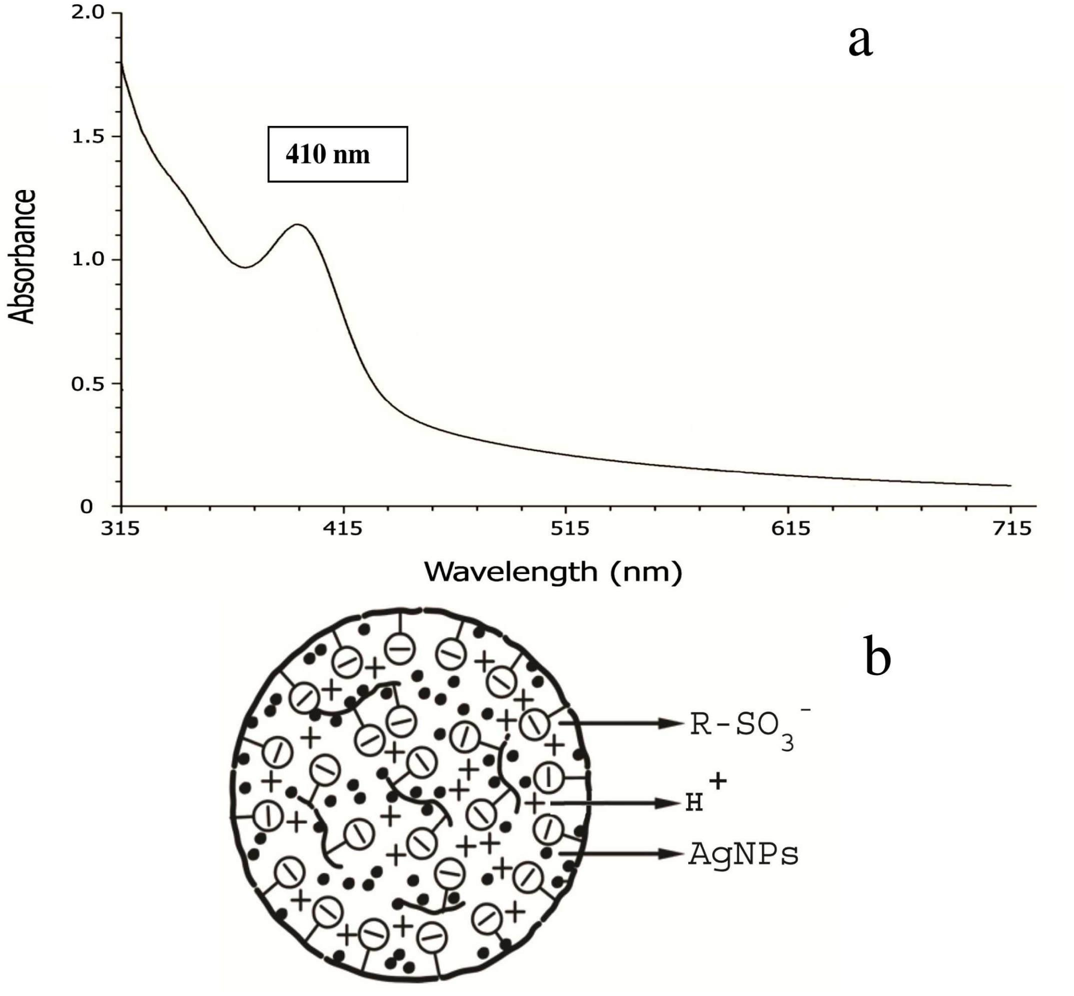


Fig.1 (a) & (b) UV–Visible spectra and the schematic structure of the PFR-AgNPs.

The FT-IR spectra of the PFR, Co (II) – PFR, PFR–AgNPs and Co (II) – PFR-AgNPs were shown in Fig.2 and Table 1. These showed a shift in wave number of dominant peaks related with the loaded metal and confirmed the metal binding process occurring at the exterior of resin [15]. This information gives confirmation that the functional groups of SO_3^- are implied in binding the Co (II) ions onto the ion exchange resins (IERs), which distorted the novel power

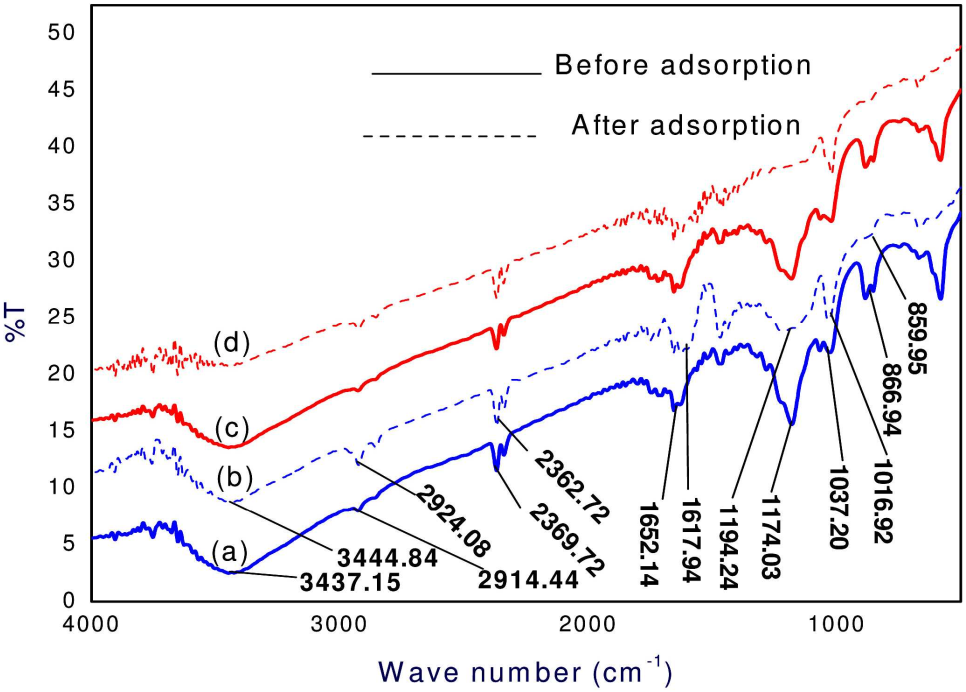


Fig.2 (a), (b), (c) and (d) IR spectra of the free and Co^{2+} loaded PFR and PFR–AgNPs

of the sulphonic groups. SEM images of the free and Co^{2+} loaded adsorbents are shown in Fig 3a, 3b, 3c and 3d respectively. As observed from Figures, a visible change of the surface morphology in the Co (II) loaded PFR and PFR-AgNPs exhibited that the adsorption of Co (II) ions has happened on the resin. The SEM-EDAX spectrum of free and Co (II) loaded adsorbent are shown in Fig 4a, 4b, 4c and 4d. The presence of Co (II) peaks in the spectrum after adsorption confirms the adsorption of Co (II) onto PFR and PFR-AgNPs. The TGA (Fig.5a and 5b) & DTA (Fig.6a and 6b) analysis of the free and Co^{2+} loaded PFR-AgNPs indicated a shift in temperature dominant peaks correlated with the loaded metal. This shift in temperature evidenced the metal binding process at the surface of PFR-AgNPs.

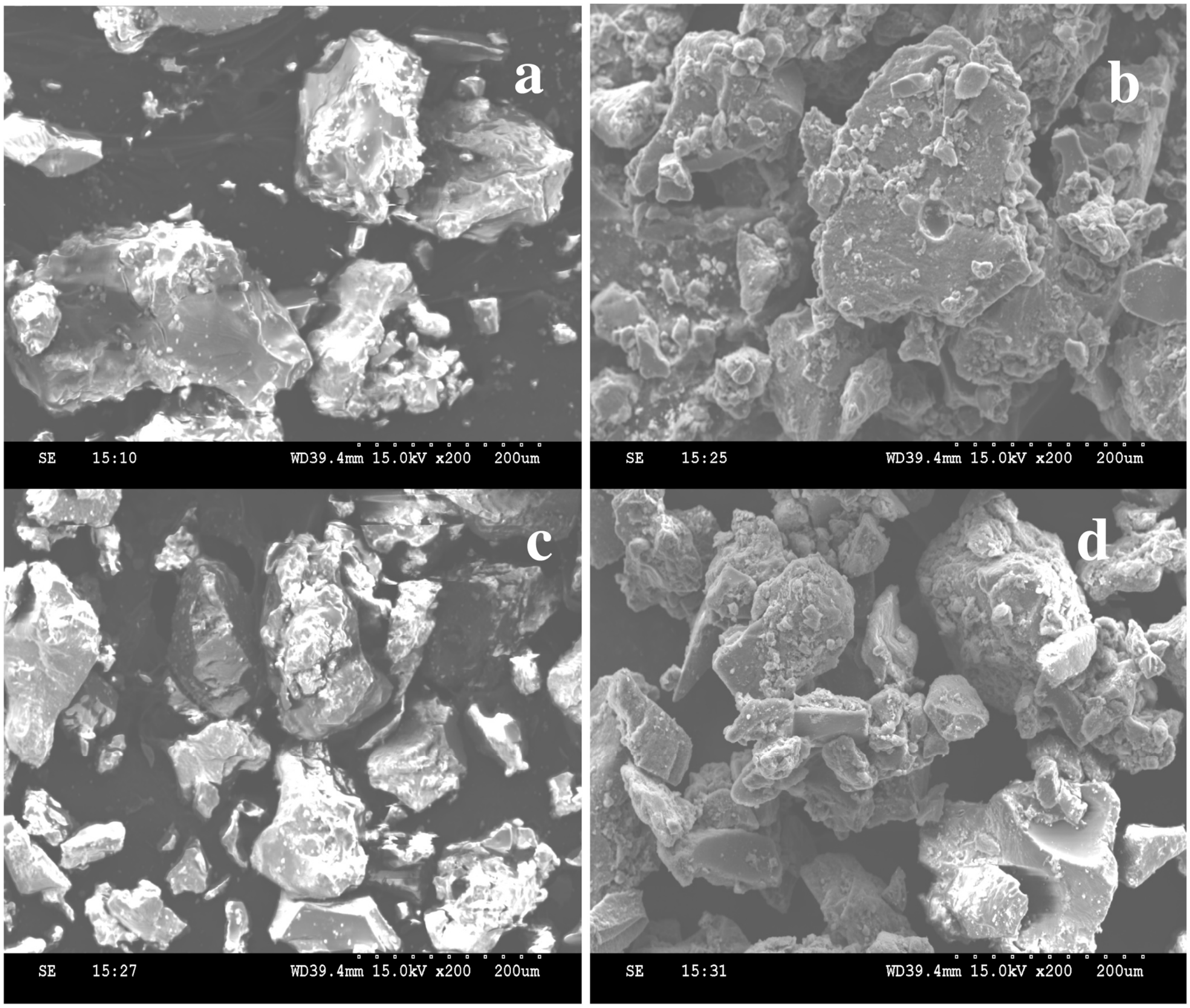


Fig.3 (a), (b), (c) and (d) SEM analysis of the free and Co^{2+} loaded PFR and PFR–AgNPs

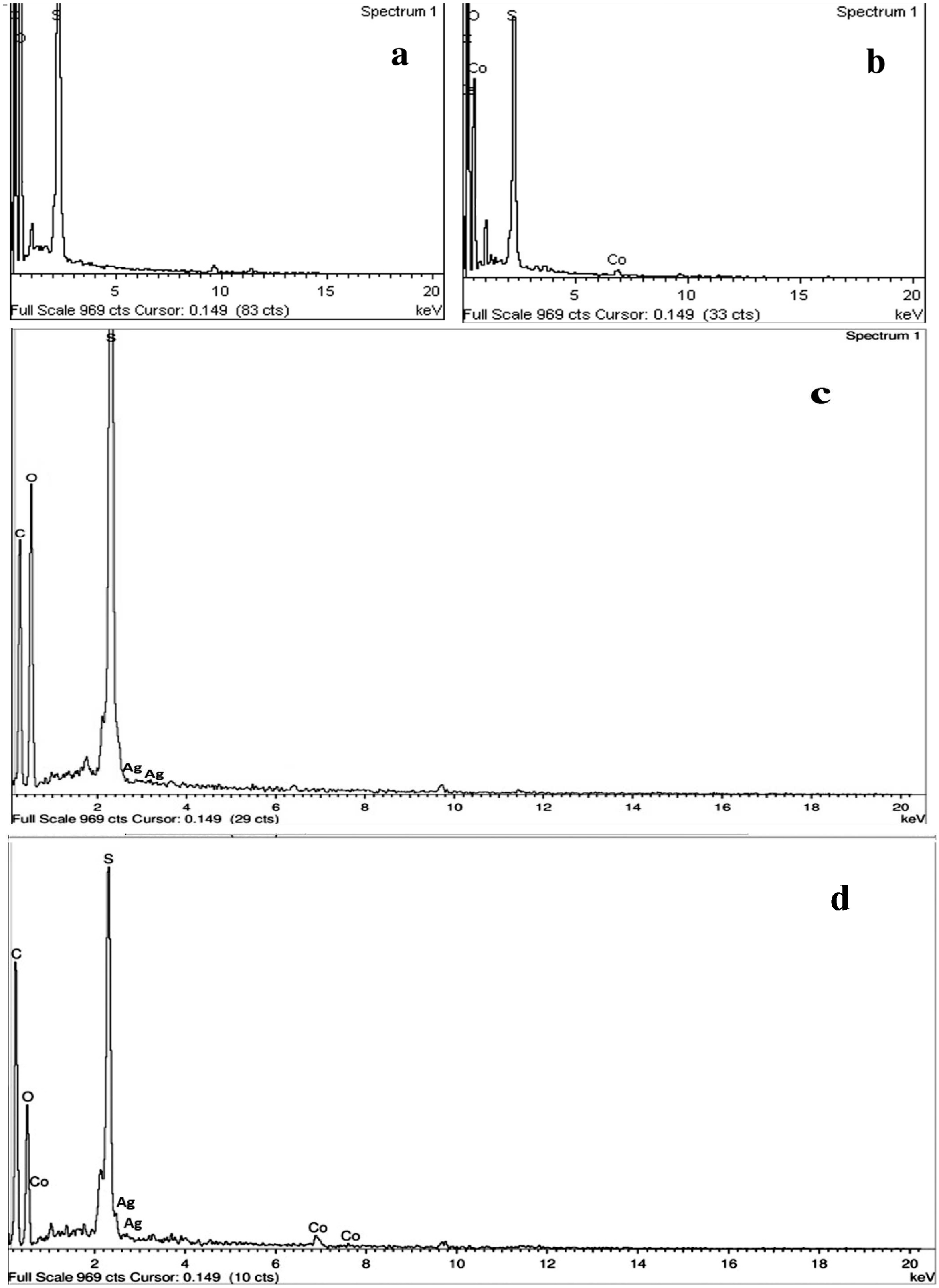


Fig. 4 (a), (b), (c) and (d) EDX spectra of the free and Co^{2+} loaded PFR and PFR–AgNPs

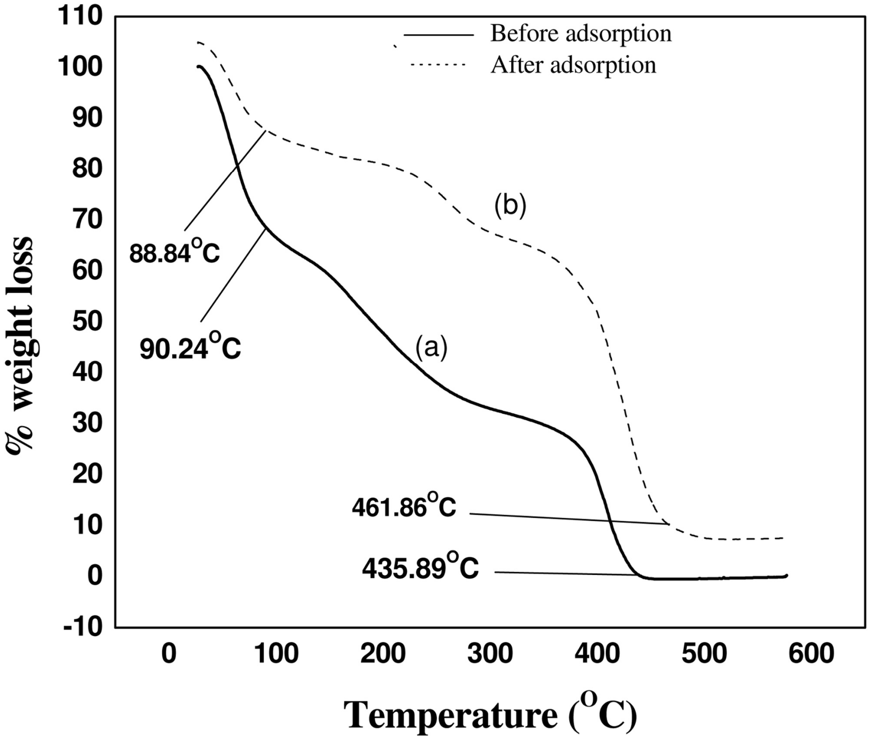


Fig.5 (a) and (b) TGA analysis of free and Co^{2+} loaded PFR-AgNPs

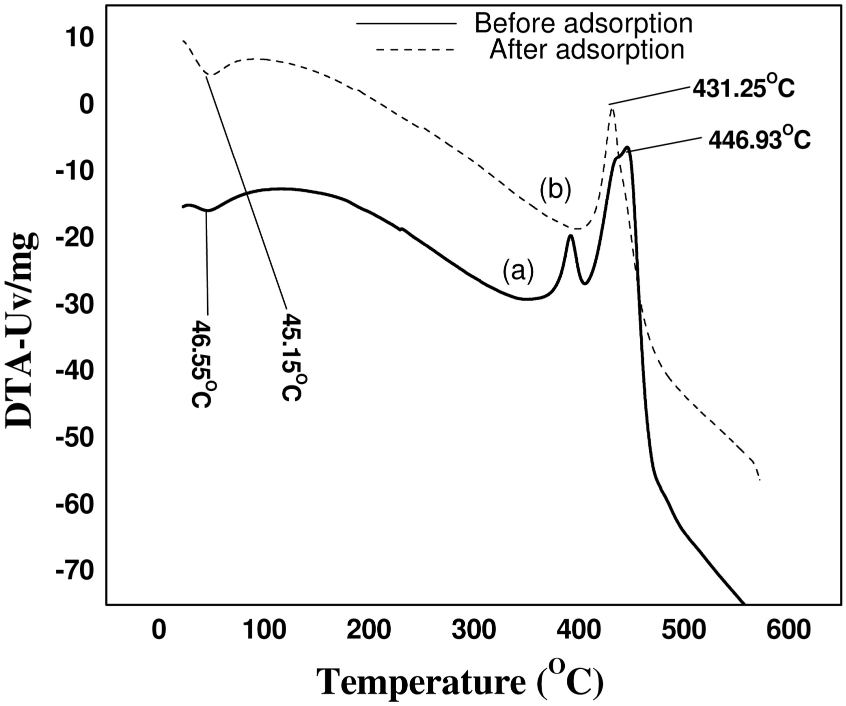


Fig.6 (a) and (b) DTA analysis of free and Co^{2+} loaded PFR-AgNPs

3.2. Effect of contact time and initial Co (II) concentration on the Co^{2+} retention:

Fig.7 tells that the time dependant performance of the removal of Co (II) from aqueous media by the IERs. This indicates clearly that the removal quantity of Co (II) increased as the contact time onwards. The equilibrium time was attained within 30 min. The primary adsorption rate was very fast which perhaps caused by the subsistence of larger number of adsorbent sites available for Co^{2+} removal from aqueous solution. While the residual available surface areas decreases, the adsorption rate slowed down may be caused by the development of repulsive forces between the Co (II) ions on the solid surface and in the liquid phase. Fig. 8 showed that the adsorption of Co (II) onto the PFR-AgNPs has been increased with increase in the initial metal ion concentration in the range 30 to 150 mg L^{-1} due to the increase in driving force caused by concentration gradient developed between the bulk solution and surface of the PFR-AgNPs. Thus the developed PFR-AgNPs can be competently used for the removal of high concentration Co (II) from aqueous solution [16].

3.3. Adsorption isotherms

The Langmuir equation says that the solid surface has a limited number of consistent sites and these are actively uniform and a monolayer is created when the solid surface reaches saturation. The Langmuir isotherm model is expressed by the following equation [17]:

$$\textbf{Langmuir isotherm} \quad : (C_e / q_e) = (1 / Q_o b) + (C_e / Q_o) \quad \text{--------} \ (3)$$

Where q_e (mg g^{-1}) is the adsorbed amount of Co (II) at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of Co (II), Q_o (mg g^{-1}) and b (g L^{-1}) are Langmuir constants related to adsorption capacity and energy of adsorption. The graph C_e/q_e against C_e (Fig.9) gave a straight line viewing the validity of Langmuir isotherm. The values of Q_o and b are found from slope and intercept of the plot and are mentioned in Table 2. The important characteristics of the Langmuir isotherm can be expressed by the equilibrium parameter R_L, which absolutely decides the favorability and nature of the isotherm of the adsorption process by the following equation.

$$\mathbf{R_L = 1/\ (1+bQ_o)\quad ---------- (4)}$$

Table 1 IR Spectral Studies (ν in cm^{-1})

Assignment	PFR	PFR-Co	PFR-AgNPs	PFR-AgNPs-Co
S=O str	1037	1016	1035	1034
SO_2 str	1176-1286	1267	1228	-------
C-S str	578-667	588-669	590-671	671
Bonded –OH str	3437	3444	3409	3404
C-C str	1652	1617	1658	1624
CH_2 bending	866	859	852	864
C=O str	1701-1747	1693-1741	1701-1745	1743
C-O str	1174	1194	1024-1524	--------
C-H str	2914	2924	2854-2924	2854-2924
C-H bending	1338-1458	1336-1454	1338-1456	1321-1456

The R_L value decides the nature and the feasibility of adsorption process are presented in Table 2. Since the R_L values found lies between 0 and 1, the adsorption process is favorable.

This isotherm is an empirical equation derived from the sorption on a heterogeneous surface signifying that binding sites are not equivalent as well as the sorbent has a surface with a non-uniform distribution of sorption heat. The equations of the Freundlich isotherm model [18] in linear forms are expressed as:

$$\textbf{Freundlich isotherm} \quad : \ \mathbf{\log q_e = \log K_F + (1/n) \log C_e\ ------- (5)}$$

Where K_F (mg g^{-1}) is the Freundlich constant and 'n' the freundlich exponent. Where q_e (mg g^{-1}) is the adsorbed amount of Co (II) at equilibrium and C_e (mg L^{-1}) is the equilibrium concentration

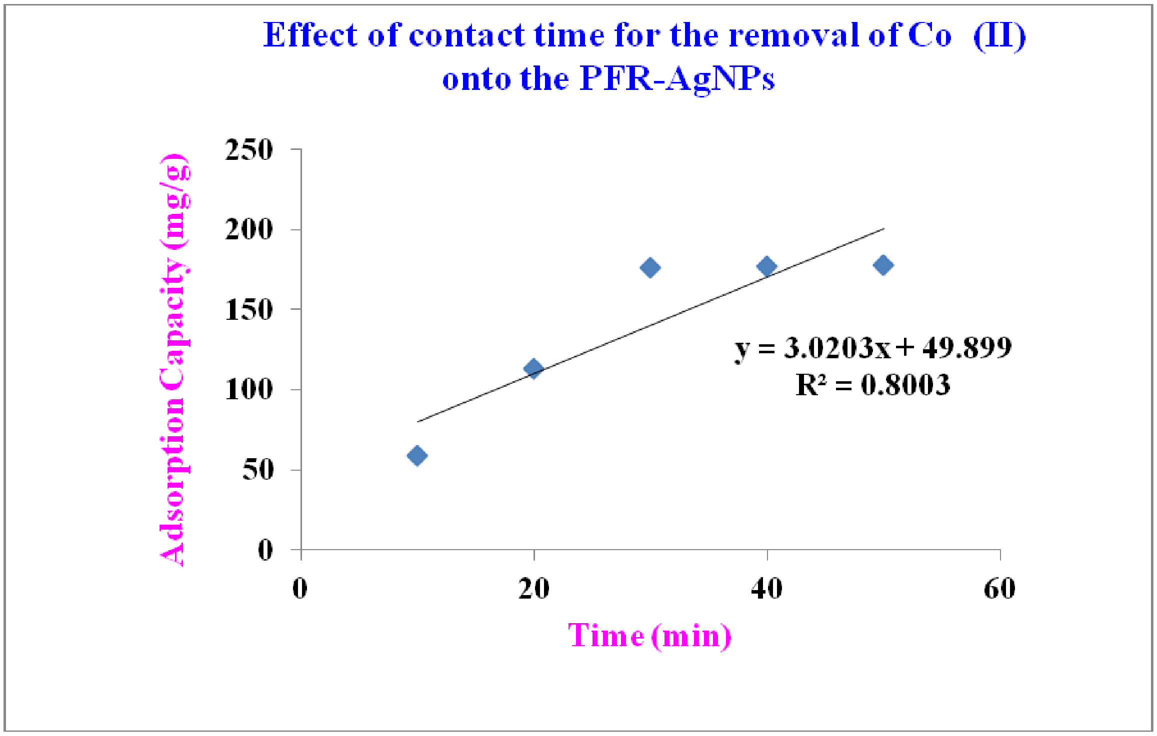


Fig.7. Effect of contact time on the removal of Co (II) from aqueous solution

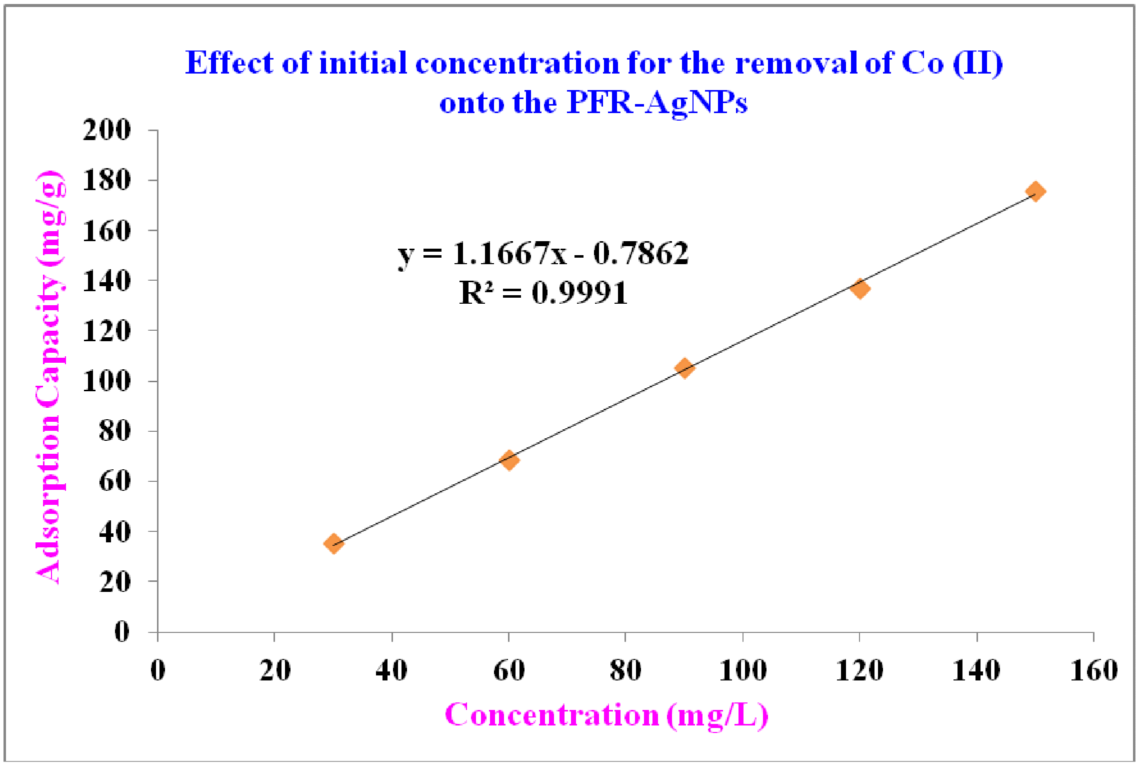


Fig.8. Effect of initial concentration on the removal of Co (II) from aqueous solution

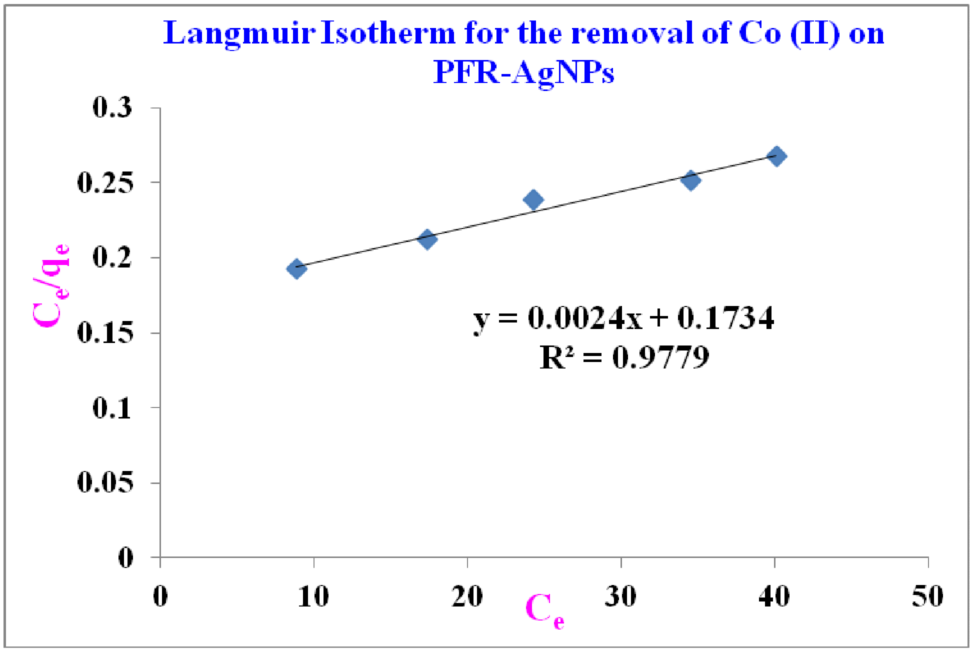


Fig.9. Langmuir plots for the removal of Co (II) from aqueous solution

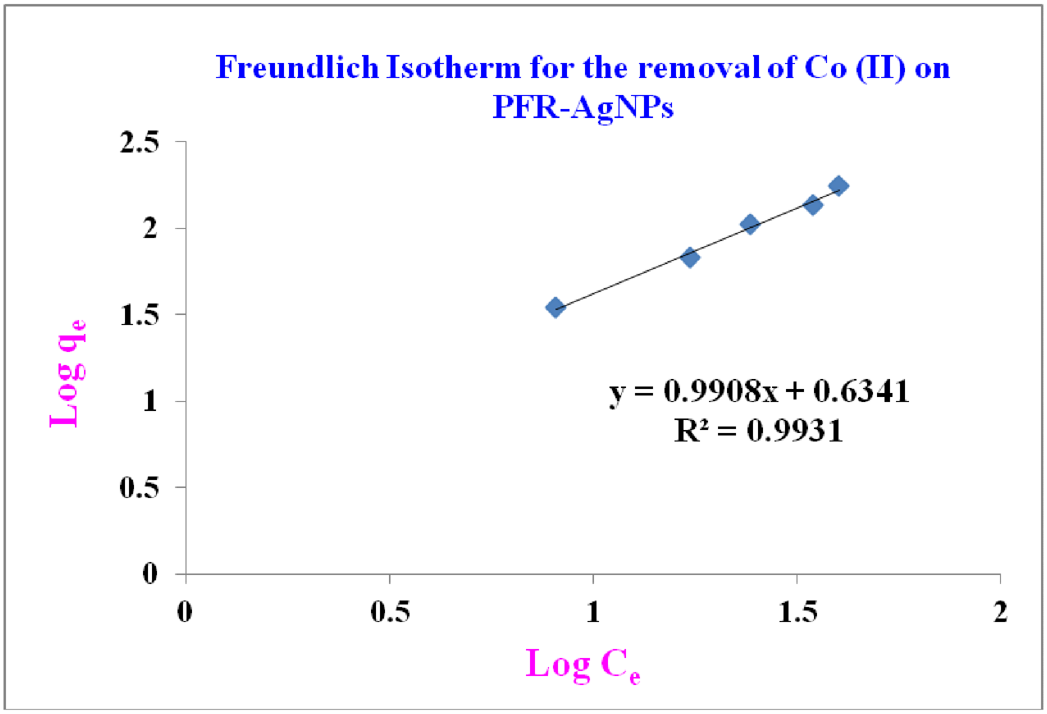


Fig.10. Freundlich plots for the removal of Co (II) from aqueous solution

of Co (II). From Fig.10, the all values are calculated and reported in Table 2. The n value was 1.0093 significant that PFR-AgNPs is better adsorbent Co (II) retention from aqueous solution.

Table 2 Adsorption isotherm parameters for the Co (II) retention

Metal ion	Langmuir				Freundlich		
	Q_o (mg/g)	b (g/L)	R_L=1/1+Q_ob	R^2	N	K_F	R^2
Co (II)	416	0.0004	0.873	0.9776	1.0093	4.3063	0.9931

3.4. Adsorption Kinetics and Intraparticle diffusion rate

The efficiency of the IERs was valued through analyzing adsorption kinetics. The rate constant was calculated from Lagergren Pseudo - first order equation which is commonly expressed as [19].

$$\mathbf{Log\ (q_e - q_t) = log\ q_e - [K_1 / 2.303]\ t\ \text{--------------}\ (6)}$$

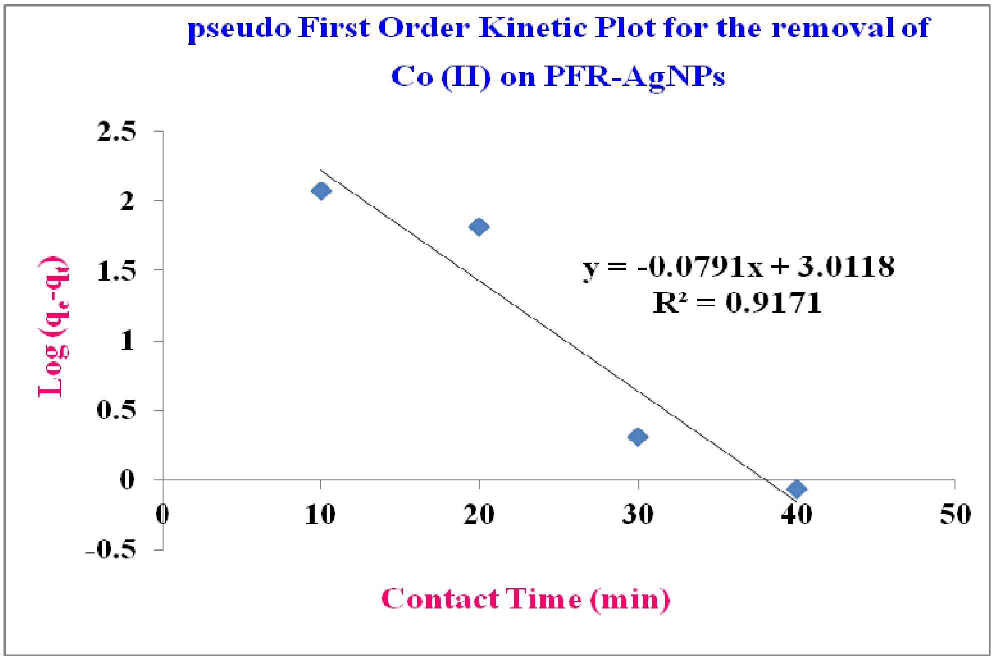


Fig.11. Pseudo first order plot for the removal of Co (II) from aqueous solution

Table 3 The kinetic parameters for the Co (II) retention

Metal ion	**Experimental q_e (mg/g)**	**Pseudo-I-Order constants**			**Pseudo-II-Order constants**		
		q_e (mg/g)	**K_1 (min^{-1})**	**R^2**	**q_e (mg/g)**	**K_2 (g/mg/min)**	**R^2**
Co (II)	175.82	1027	0.1821	0.9171	476	3.12×10^{-5}	0.97

Where K_1 is the pseudo-first-order rate constant (min^{-1}) and q_e (mg g^{-1}) is the adsorption capacity at equilibrium and q_t (mg g^{-1}) is the adsorbed amount of metal ion after time t (min). The all values are calculated from Fig.11 and are presented in Table.3.

The linear form of Ho pseudo - second order kinetic model can be expressed as [20]:

$$t / q_t = 1/ K_2 q_e^2 + t/q_e \text{ -------------- (7)}$$

Where K_2 is the rate constant of second order adsorption (g/mg/min). K_2 and q_e were determined from the Fig.12 and are tabulated in Table.3. The R^2 values for pseudo second-order kinetic model are relatively higher than pseudo-first order kinetic model. The correlation between predicted and experimental q_e values pointed out that the adsorption system studied goes to pseudo second-order kinetic model.

This model was to the highlight the rate-limiting step of the adsorption process and recommended by Weber and Morris [21]. If the plot q_t versus $t_{1/2}$ makes a straight line and exceed throughout the origin, intra-particle diffusion is the source of rate-limiting step. This equation can be expressed as

$$q_t = K_{id} t^{1/2} + C \text{ -------------- (8)}$$

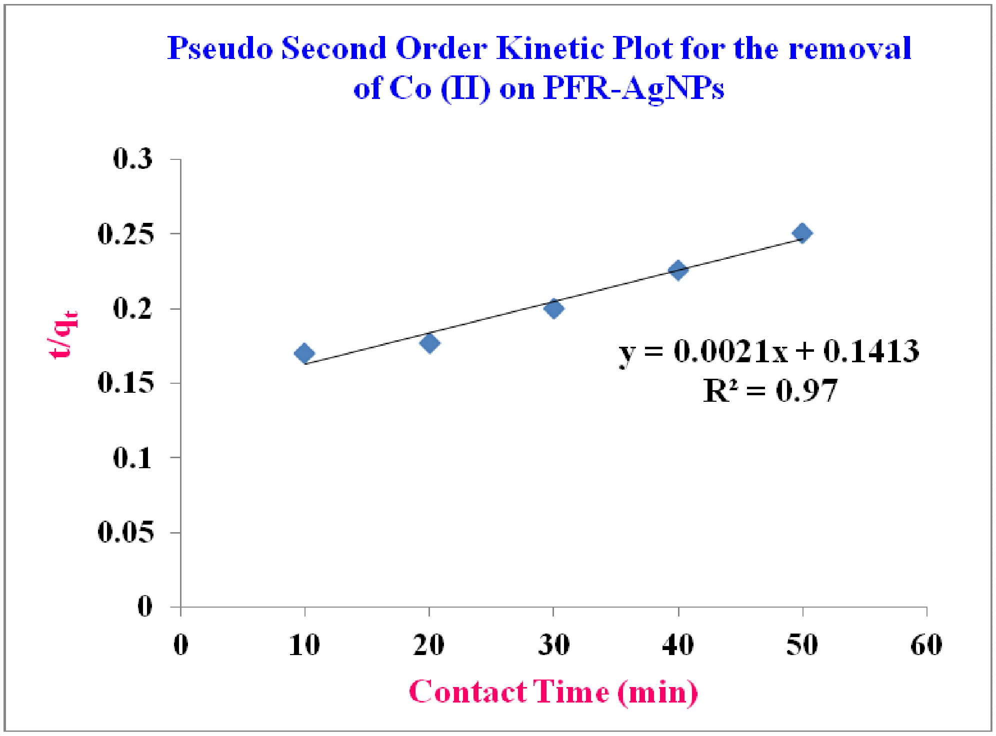


Fig.12. Pseudo second order plot for the removal of Co (II) from aqueous solution

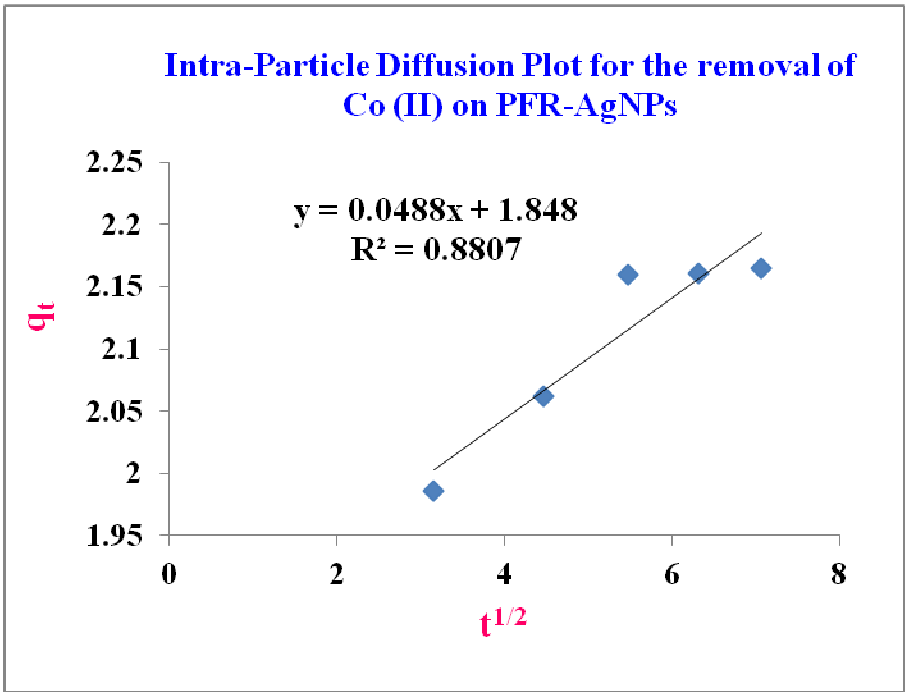


Fig.13. Intraparticle diffusion model for the Co (II) retention.

Table 4 The intraparticle diffusion parameters for the Co (II) retention

Metal ion	Intraparticle diffusion model		
	K_{id} (g mg^{-1} min$^{-1/2}$)	C	R^2
Co (II)	0.0488	1.848	0.8807

Where q_t is the adsorption capacity at any time t and K_{id} is the intra particle diffusion rate constant and C is the film thickness. From Fig.13, the calculated K_{id}, C and correlation coefficient (R^2) values are tabulated in Table.4. Larger the value of C greater is the effect of boundary layer on adsorption process. The deviation of the plot from the linearity indicates the rate-limiting step have to be controlled boundary layer diffusion. Fig.13 shows that the plots contain multi-linear portions suggests that the two or more steps direct the sorption process. These two straight lines describe the points, the sharp first linear portion is because of the film diffusion and the second linear portion is because of the pore diffusion. Non-linearity of the plots had revealed the multi stage adsorption for adsorbing Co^{2+} ions through PFR-AgNPs.

3.5. Effect of temperature:

The effect of temperature on the adsorption of Co (II) by PFR-AgNPs was studied form 303 K to 323 K. Thermodynamic parameters tell feasibility and the spontaneous nature of the adsorption process. The thermodynamic parameters, specifically free energy change (ΔG^O), entropy change (ΔS^O) and enthalpy change (ΔH^O), were studied using the equilibrium constants at different temperatures. The adsorption equilibrium constant (K_C) was calculated by the following equation:

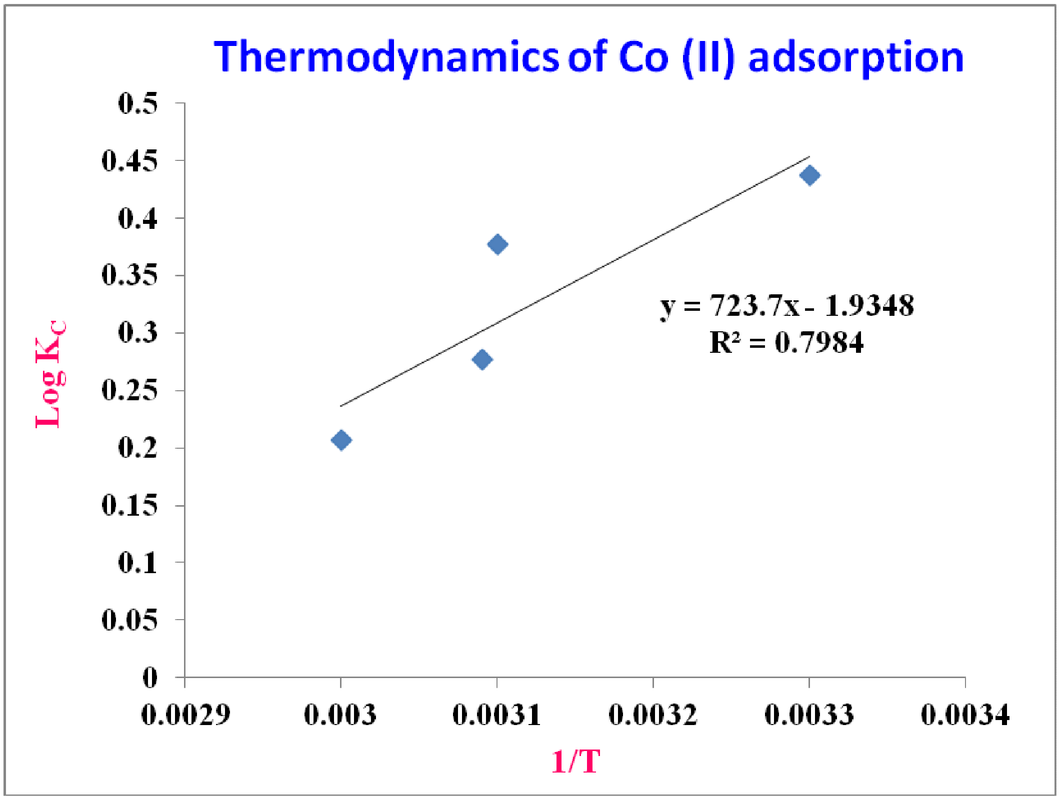


Fig.14. Thermodynamics of Co (II) adsorption onto the PFR-AgNPs.

Table 5 Thermodynamic parameters for the Co (II) retention

Temperature	**$-\Delta G^O$ ($kJ\ mol^{-1}$)**				**$-\Delta S^O$ ($J\ mol^{-1}\ K^{-1}$)**	**$-\Delta H^O$ ($kJ\ mol^{-1}$)**
	303 K	**313 K**	**323 K**	**333 K**		
Co (II)	2539	2260	1716	1321	37.04	13843

$$K_C = C_{ad}\,(solid) / C_e\,(solution) \quad \text{-------------} \ (9)$$

C_{ad} is the amount of metal (mg) adsorbed on the adsorbent per liter (L) of the solution at equilibrium, and C_e is the equilibrium concentration (mg L^{-1}) of the metal in the solution. The free energy change (ΔG^O) of the adsorption was calculated by the following equation:

$$\Delta G^O = -2.303\ RT \log K_C \quad \text{--------------} \ (10)$$

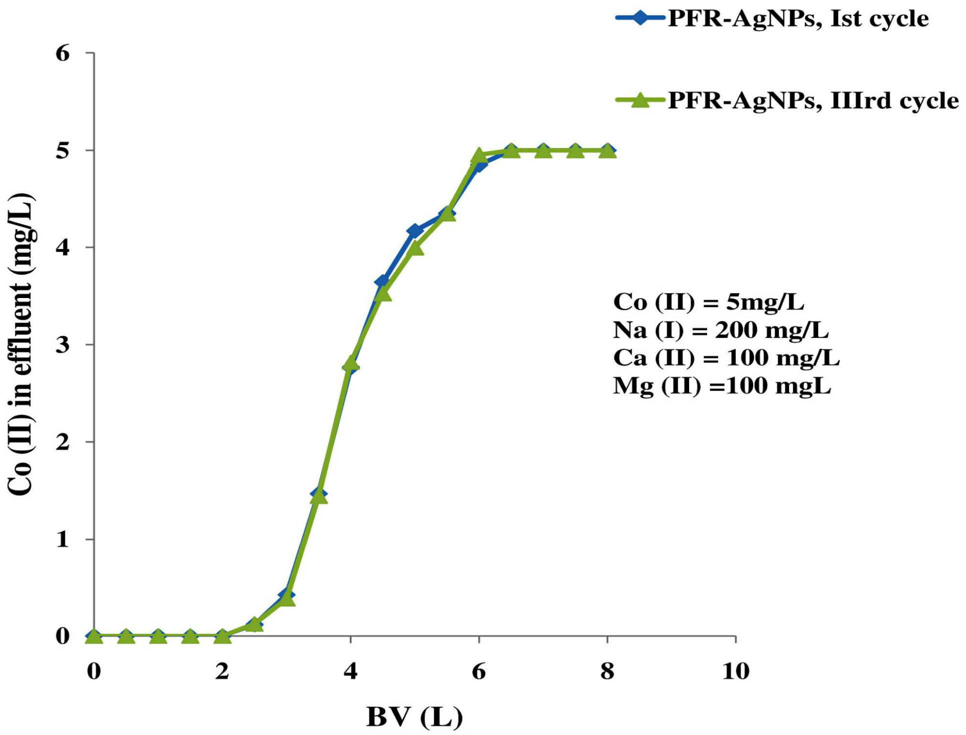
The correlation between equilibrium constant (K_C) and temperature (T) is indicated using the van't Hoff equation:

$$\mathbf{Log\ K_C = - [\Delta H^O / 2.303\ RT] + (\Delta S^O / 2.303R) \quad ------------- (11)}$$

The enthalpy change (ΔH^O) and entropy change (ΔS^O) values were calculated from the slope and intercept of the linear plot log K_C versus 1/T (Fig.14). The calculated all values were tabulated in Table.5. The negative values of ΔH^O show the exothermic nature of the ion exchange process between C_O (II) and PFR-AgNPs, as the negative value of ΔG^O indicates the spontaneous nature of Co (II) sorption [22]. The negative entropy change (ΔS^O) value represents to a decrease in the degree of freedom of the adsorbed metal ions.

3.6. Column studies:

The breakthrough curve is especially main features for finding out the process and the dynamic reaction of adsorption in a fixed-bed column [23]. The uninterrupted adsorption of Co^{2+} on PFR and PFR-AgNPs was studied in the presence of competing ions like Na^+, Ca^{2+} and Mg^{2+} by a research laboratory scale in a fixed-bed. The breakthrough time and exhaustion time for Co^{2+} ion was found [24] and shown in Fig.15 and the PFR was also needed for reference. It was indicated that the Co (II) breaks through rapidly on the PFR due to its scanty selectivity towards cobalt and the effective treatment volume is almost 900 bed volumes (BV). On the contrary, appropriate breakthrough results were determined for PFR-AgNPs as about 6000 BV in identical conditions due to the immobilized negatively charged sulfonic acid groups bound to polymer matrix would significantly improved the permeation and preconcentration of the Co (II) from aqueous media to interior plane of the polymer [25] as well as successively make favorable conditions for Co (II) retention by AgNPs. This effect is called as potential donnan membrane effect. Besides, Co (II) can be selectively withdrawn by AgNPs particles by inner-sphere



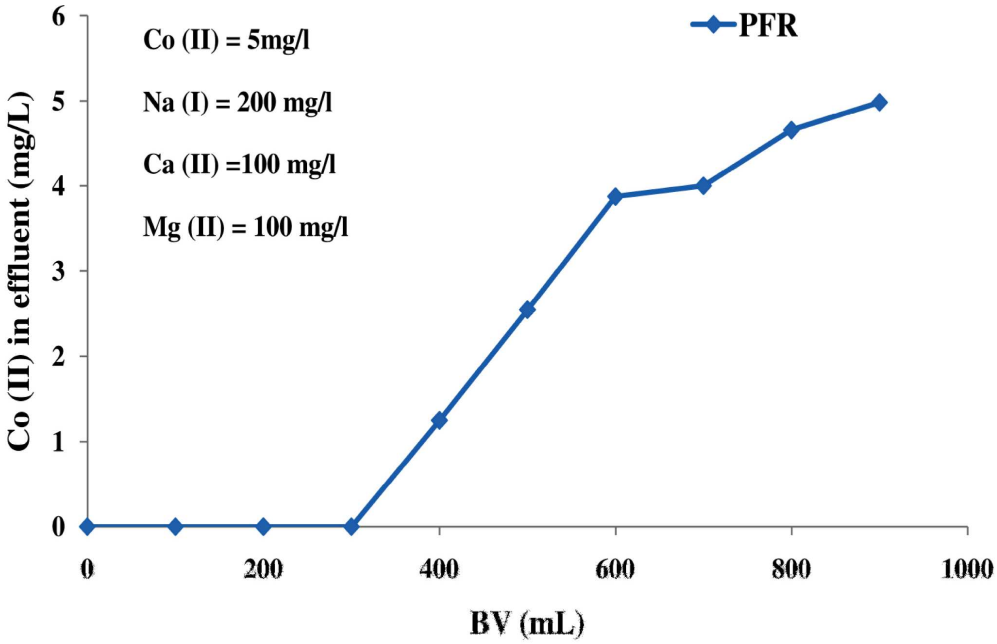


Fig.15. comparison of breakthrough curves of Co (II) adsorption by PFR-AgNPs and PFR.

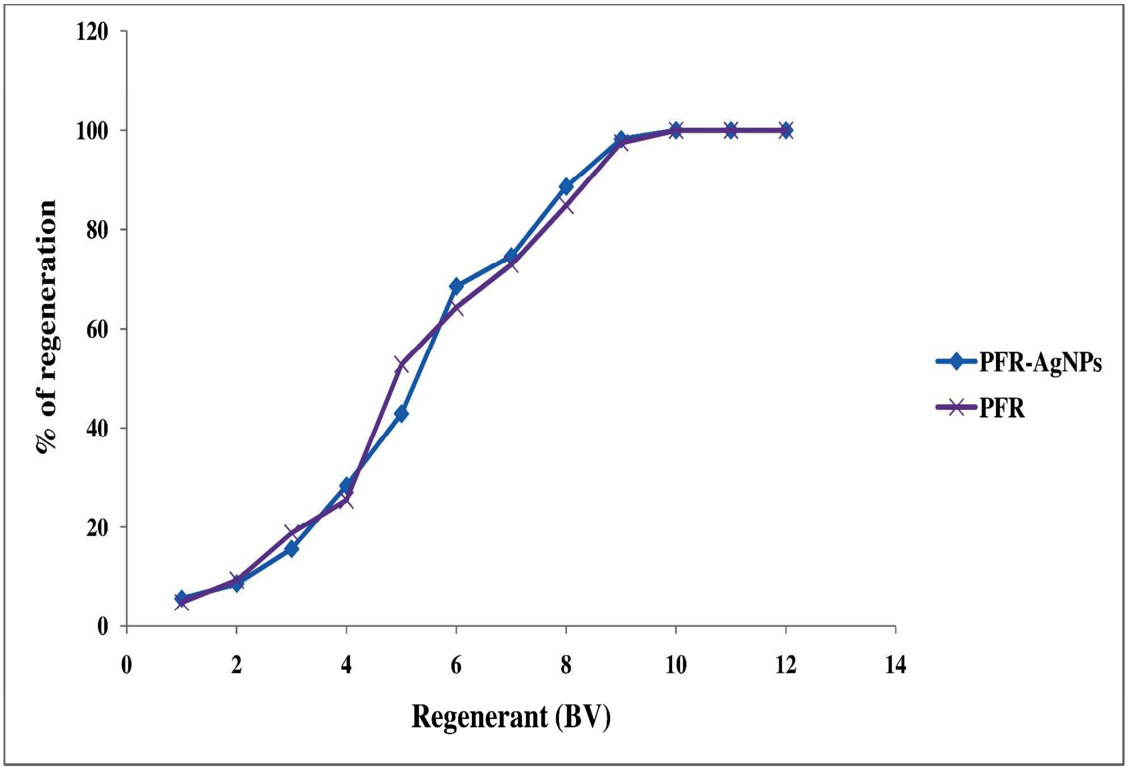


Fig.16. A column regeneration capacity of the PFR-AgNPs and PFR.

complexation of Co (II) with AgNPs [26].The cobalt concentration in the effluent reduced considerably from 5 to less than 0.05 mg/L, this limit was allowed according to Environmental Bureau of Investigation. The exhausted PFR and PFR-AgNPs column was regenerated by a 5 % (w/w) NaCl solution and the results are shown in Fig.16. It was shown that the 9-10 BV regenerates could efficiently regenerate the preloaded cobalt from the resin. Also, we carried out continuous adsorption– regeneration cycles that run for PFR-AgNPs bed-column to confirm its feasibility for future application studies. The imbrications of cobalt breakthrough curves for the 1st and 3rd cycle confirmed that PFR-AgNPs can be utilized for repetitive use without noticeable capacity loss after regeneration by 5 % NaCl solution. It was also noted down that the dynamic adsorption capacities of PFR-AgNPs and PFR column towards cobalt with opposing ions (Na^+, Ca^{2+}, and Mg^{2+}) was around 141.34 and 56.72 mg g^{-1}.

Table 6 Comparison of adsorption capacities of different adsorbents with PFR-AgNPs adsorbent

Adsorbent	Co (II)	Reference
SKN1 cation exchange resin	69.4	[27]
IDA chelating resins (CR-15)	116.7	[28]
Aminophosphonic acid resin	127	[29]
Amberlite IRN-77 strong acid resin	74.6	[30]
NKC-9 strong acid resin	361	[31]
PFR-AgNPs	416	Current work

3.7. Comparison of maximum adsorption capacity of PFR-AgNPs adsorbent with some other adsorbents

The variations of metal intake were caused by the properties of adsorbents like structure, functional groups and surface area. The adsorption capacities of the PFR-AgNPs and other adsorbents for the removal of Co^{2+} from aqueous solution or wastewater were mentioned in Table 6 which showed that the adsorption capacity of the PFR-AgNPs dealt in the present work was higher than the other literature reported adsorbents [27-31].

4. Conclusion

Silver nanoparticles were tightly impregnated within a polymeric matrix PFR through a polycondensation process, using formaldehyde as the cross-linking agent and a novel composite macro porous cation exchanger PFR-AgNPs was obtainable for selective Co (II) removal based on Donnan membrane principle in the presence of competing ions like Na^{2+}, Ca^{2+} and Mg^{2+}. As Compared to PFR, PFR-AgNPs displayed more preferable Co^{2+} confiscation from aqueous medium due to the potential donnan membrane effect applied by impregnating AgNPs. The kinetic studies show that the adsorption of Co^{2+} onto PFR-AgNPs followed the pseudo-second order rate expression. The adsorption isotherm studies confirmed a good fit with the Freundlich isotherm model. The exchanges between Co (II) and PFR-AgNPs are thermodynamically favorable and exothermic in nature. The exhausted adsorbents are effectively regenerated by using the 5 % (w/w) NaCl. The current study concludes that macro porous cation exchange resin PFR-AgNPs could be applied for the removal of cobalt from aqueous solution as well as waste water.

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Selective Co (II) Removal from Aqueous Media by Immobilizing the Silver Nanoparticles within a Polymer-Matrix through Formaldehyde Cross Linking Agent

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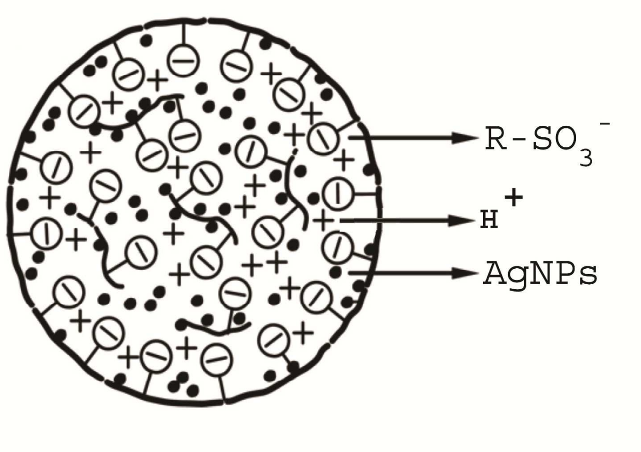

Fig. The schematic structure of the PFR-AgNPs.