

Research Article

Studies on Adsorption and Ion Exchange properties of Poly-o-Toluidine Cerium(IV) Iodate Nanocomposite Exchanger for the Removal of 2,4,6 Trinitrophenol and Mercury Ions

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Abstract

The present paper summarises the synthesis, characterisation and applications of Poly-o-toluidine cerium(IV) iodate nanocomposite exchanger. The material showed high affinity for Hg(II) ions. Some important binary separations and quantitative separation of Hg(II) ions were achieved using the exchanger. The material was effectively used for the adsorption of 2,4,6 trinitrophenol. Various factors affecting the adsorption such as time, temperature, pH and the interference of other metal ions on adsorption were also studied. Significant removal of about 95% was attained using the nanocomposite.

Keywords: Poly-o-toluidine, nanocomposite, mercury, 2,4,6 trinitrophenol, adsorption

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Introduction

The ever increasing needs of the human population lead to the development of various industries which directly or indirectly discharges contaminants to the environment. Industrial effluents mainly contain organic contaminants and heavy metal ions, which even at low concentration causes high toxicity to humans, flora and fauna. Toxic heavy metals of significant concern include mercury, lead, cadmium, nickel, chromium, arsenic etc which are listed as priority pollutants by the US Environmental Protection Agency (EPA). Phenols and its derivatives, nitroaromatic compounds, benzene and its derivatives etc are the organic priority pollutants listed by EPA. Although adverse health effects of the pollutants have been known for a long time, exposure to pollutants continues and is even increasing. Adsorption, advanced chemical oxidation, biodegradation, ultrasonication, photodegradation etc are the common methods followed for the removal of organic pollutants and ion exchanging, chemical precipitation, electrochemical method etc are used for the removal and separation of heavy metals in the past decades [1-5].

The present study deals with the use of nanocomposite ion exchangers for the removal of organic pollutants and heavy metal ions. Nanocomposite ion exchangers are hybrid materials having a polymeric organic part and an inorganic counterpart. Usually the inorganic part is embedded on to the polymeric species. The properties of both organic and inorganic constituents bring enhanced properties to the material [6]. The porous nature of the polymeric part makes it suitable for adsorption applications and the exchange properties of the inorganic counterpart make it an efficient ion exchanger. Hence it can be effectively used for the removal of organic pollutants and heavy metal ions. In this context, novel poly-o-toluidine cerium(IV) iodate (POT CeI), nanocomposite exchanger was synthesised and characterised. The utility of the material is brought out by studying the adsorption of 2,4,6-trinitrophenol (TNP) and also the removal of Hg(II) ions by ion exchange from aqueous solutions.

2,4,6-trinitrophenol is a nitroaromatic compound which is associated with many industrial and chemical processes. It is used in electric batteries, leather industry, pesticides, dyes, pharmaceuticals, paints, textile mordents, as a laboratory reagent, in matches and explosives etc. It is highly reactive with wide variety of materials like concrete, plaster, bases, metals like zinc, copper, mercury etc. TNP is one of the main propellants used as fuel oxidants for ammunitions [7]. The dangers of TNP include damage of internal organs, respiratory depression and even death. They are highly mobile and persistent in ground water and do not undergo degradation easily [8]. Studies on adsorption of TNP using amberlite resins, bentonite and mesoporous silica have been reported [9-11]. Use of biosorbents and biodegradation of TNP using bacterial strains were the other techniques studied [12-13]. So far no studies have been carried out using composite exchangers for the removal of TNP. The effect of various factors on

adsorption like pH of the solution, contact time, temperature and interference of other metal ions on adsorption were also studied. Along with the study of adsorption of TNP, the ion exchange capability of the material for Hg(II) ions were also carried out and studied. Some important binary separations using synthetic mixtures were also achieved using the exchanger.

Experimental

Chemicals and Reagents

The main reagents used were Ceric ammonium nitrate (E.Merck), Potassium iodate (Loba Chemie, India), Poly-o-toluidine (Loba Chemie, India), 2,4,6 trinitrophenol (Loba Chemie, India). All other reagents and chemicals used for the synthesis were of analytical grade.

Instrumentation

FTIR spectrometer model Thermo Nicolet Avtar370 was used for IR studies, X-ray diffractometer Bruker AXS D8 Advance for X-ray diffraction studies with Cu K α radiations, TG Perkin Elmer Diamond TG/DTA Analysis System for thermogravimetric/ derivative thermogravimetric analysis were used at a rate of 10°C in nitrogen atmosphere, Jeol Model JSM - 6390LV for Scanning Electron Microscopic analysis and UV-Visible spectrophotometer model JASCO V660 was used for spectrophotometric measurements.

Synthesis of Nanocomposite Exchanger

Synthesis of Poly-o-toluidine

Poly-o-toluidine was prepared by mixing similar volume ratios of 0.4 M ammonium persulfate prepared in 4.0 M HCl into 10% o-toluidine prepared in 2.0 M HCl with continuous stirring by a magnetic stirrer for 2 hours at 0°C; a green coloured gel was obtained. The gel was kept for 24 hours at 0°C [14].

Synthesis of Cerium(IV) iodate

The synthesis of the inorganic precipitate of cerium(IV) iodate was carried out by mixing 0.05 M Potassium iodate solution into 0.05 M Ceric ammonium nitrate in 2:1 ratio respectively. The pH of the solution was maintained at 2 and the mixing was carried out under constant stirring at room temperature. The yellow coloured gel formed was kept for digestion for 24 hours at room temperature.

Synthesis of Poly-o-toluidine cerium(IV) iodate nanocomposite (POT CeI)

The synthesis of Poly-o-toluidine cerium(IV) iodate nanocomposite was carried out by simple stirring process. The ex-situ polymerised gels of poly-o-toluidine were added to the yellow inorganic precipitate of cerium(IV) iodate and mixed thoroughly with constant stirring resulting in the formation of green coloured slurry. The green coloured slurry was kept for digestion at room temperature for 24 hours. The supernatant liquid was decanted and the gel was filtered. The excess acid was removed by washing with demineralised water (DMW) and the material was dried in an air oven at 30 °C. The dried products were immersed in DMW to obtain small granules. They were converted to H⁺ form by treating with 1.0 M HNO₃ for 24 hours with occasional shaking, intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed with DMW and then dried at 30 °C and was kept in desiccator.

Ion Exchange Capacity (IEC)

The ion exchange capacity of the material was determined by column method. 1 g of the material in H⁺ form was taken in a glass column of 1.1 cm diameter plugged with cotton wool at the bottom. 100 mL of 1.0 M NaCl solution was used to elute the H⁺ from the exchanger. The flow was maintained at a rate of 1 mL min⁻¹. The H⁺ ion content of the effluent was then determined by titrating it against a standard solution of 0.05M NaOH solution. The ion exchange capacity in meqg⁻¹ was calculated using the formula,

$$IEC = av/w$$

where a is the molarity and v is the volume of alkali used during titration and w is the weight of the exchanger taken [15].

Distribution Studies

Distribution coefficient, K_d is defined as the ratio of the concentration of the metal ion in the exchanger and in the solution. Distribution studies were carried out for various metal ions in demineralised water by batch process. In this method, 0.1 g of the exchanger was equilibrated with 20 mL of the metal ion solutions for 24 hours at room temperature. The metal ion concentrations before and after sorption were determined spectrophotometrically/complexometric titration against standard EDTA solution. In the complexometric method, the K_d values were calculated using the formula,

$$K_d = \frac{(I - F)}{F} \times \frac{V}{W}$$

where, I is the initial volume of EDTA used, F is the final volume of EDTA used, V is the volume of the metal ion solution (mL) and W is the weight of the exchanger [15].

Binary Separation

Quantitative separations of some metal ions were achieved by Poly-*o*-toluidine cerium(IV) iodate exchanger. 1 g of exchanger in H^+ form was packed in a glass column with a glass wool support at the bottom. The column was washed thoroughly with demineralized water and the mixture of two metal ions (each with initial concentration of 0.1 mol L^{-1}) were loaded onto it and allowed to pass through the column at a flow rate of $5\text{--}20 \text{ drops min}^{-1}$ until the level was just above the surface of the material. The process was repeated twice or thrice in order to ensure the complete sorption of metal ions on the bead. The separation of metal ions were achieved by collecting the effluent in 10 mL fraction and titrating against the standard solution of di-sodium salt of EDTA (0.01 mol L^{-1})

2,4,6-trinitrophenol Adsorption Studies

To study the TNP adsorption property of the material from aqueous solution, 0.1g of the exchanger was shaken with 10mL of 50ppm TNP at different time intervals ranging from pH 2 to 12. The temperature dependence study was carried out by shaking 10mL of TNP with 0.1g of exchanger at room temperature and at higher temperature range. The effect of contact time was studied by shaking 0.1 g of the material with 10 mL of TNP solution at different time intervals. The interference of other metal ions on the adsorption was studied by shaking 10mL of TNP solution with 5mL of metal ion solutions of Hg(II), Cu(II), Cd(II) and Co(II). In order to calculate the concentration change of TNP solution, the absorbance of the solution was determined spectrophotometrically at λ_{max} 355nm [16].

Results and Discussion

The nanocomposite exchanger, POT CeI was obtained as shining black crystalline solid. The composite exchanger showed higher ion exchange capacity of 1.84 meqg^{-1} than its inorganic counterpart, CeI which showed an exchange capacity 0.84 meqg^{-1} only.

The FT-IR spectrum of POT CeI (**Figure 1(a)**) shows a peak around 3000 cm^{-1} which may be related to the stretching of N-H bonds of benzenic and quinonic rings [17]. The peak at 2352 cm^{-1} indicates stretching frequency of $C \equiv N$ group [18]. The band near 1600 cm^{-1} can be due to the presence of interstitial water present in the composite material [19]. The additional band at around 1400 cm^{-1} can be ascertained to the stretching vibration of C-N [19]. This indicates that the material contains considerable amount of poly-*o*-toluidine in the material. An assembly of peaks in the region $800\text{--}500 \text{ cm}^{-1}$ may be ascribed to the presence of metal oxygen bonding present in the material [19].

The X-ray diffraction (**Figure 1(b)**) studies with single prominent peak shows the monocrystalline character of the material. The particle size calculated from the full width at half maximum value using Debye Scherrer equation is 4.93nm.

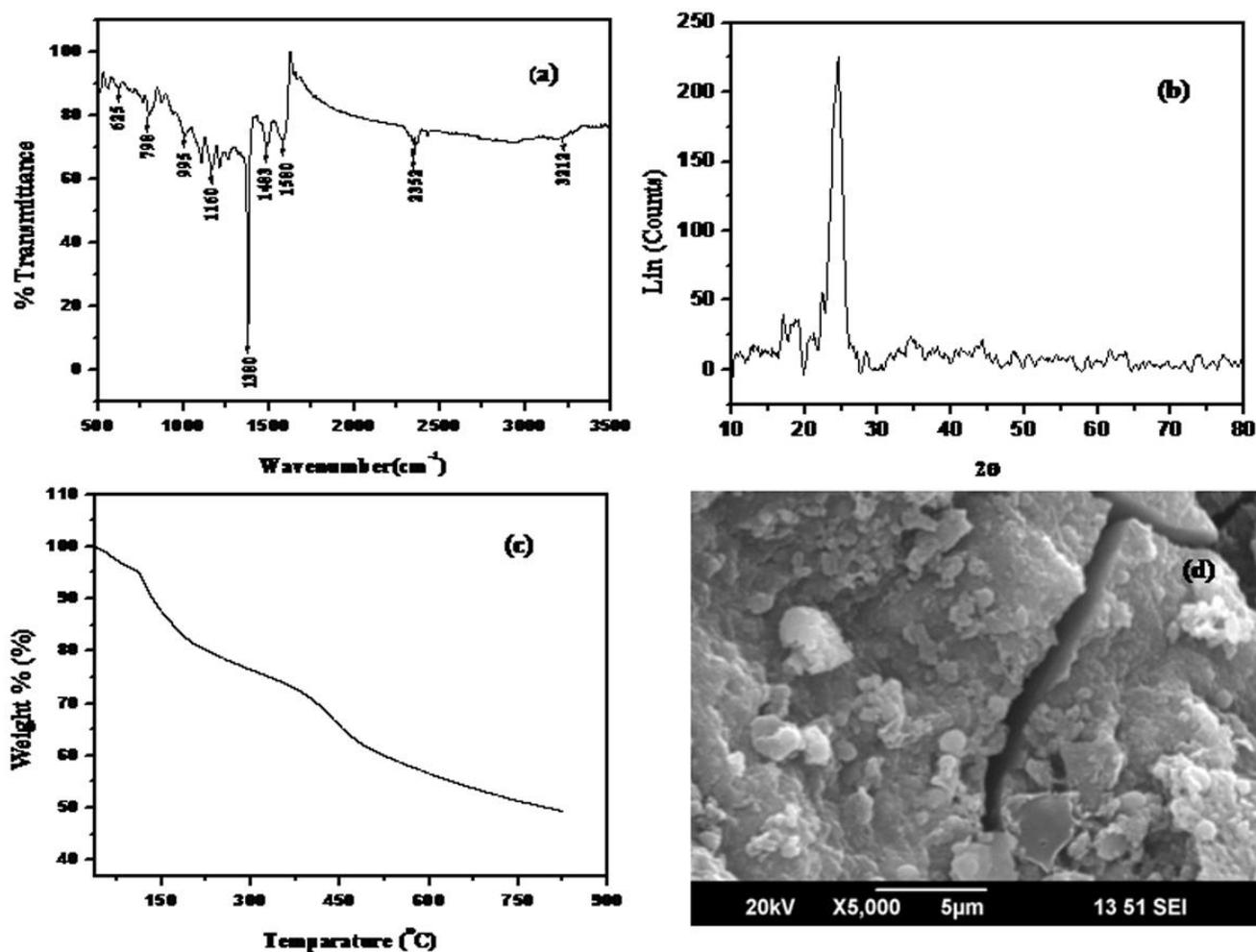


Figure 1 (a) FT-IR (b) XRD (c) TGA and (d) SEM images of POT CeI nanocomposite.

The thermogravimetric study of the material (Figure 1(c)) shows about 5% weight loss upto 100°C, which may be due to the removal of external water molecules present in the composite. Further weight loss of about 30% observed can be due to the decomposition of the organic material. As the temperature increased, gradual decomposition of the material was observed and 50% weight of the material was retained upto 800°C. The SEM image (Figure 1(d)) reveals porous and irregular surface of the material with cracks.

In order to explore the potential of the composite material in the separation of metal ions, the distribution studies for various metal ions in different solvent system were studied (**Table 1**). The distribution data shows the selectivity of the material towards Hg(II) and Bi(III) ions.

Binary Separation Studies

The distribution study data urged to carry out the binary separation of some important metal ions viz Pb(II)-Hg(II), Ni(II)-Hg(II) and Ca(II)-Hg(II) (**Table 2**). Binary separation is carried out between metals having K_d values greater than 5. Greater the separation factor, easier will be the separation. Binary separation is based on sequential elution of ions through the column; the weakly retained metal ions get eluted first, followed by the stronger one.

Mercury is a potent pollutant which does not break down easily. Once if it enters the environment from any source, it remains there. Hence the environmental and health hazards caused by mercury lead to the control and use of mercury and its associated compounds in many countries [20]. A practical application of the exchanger was demonstrated by carrying out quantitative separation of Hg(II) from wood industry effluents, where mercury is commonly found (**Table 3**).

Table 1 K_d values of exchanger for various metal ions.

Metal ion	DMW	0.001M	0.01M	0.1M	0.001M	0.01M	0.1M
		HNO ₃	HNO ₃	HNO ₃	NH ₄ NO ₃	NH ₄ NO ₃	NH ₄ NO ₃
Hg(II)	172.44	166.3	157.12	150.09	168.3	134.9	130.66
Bi(III)	154.83	140.8	135.3	120.1	143.78	133.05	110.29
Cu(II)	54.81	34.24	15.56	13.02	42.31	38.6	10.5
Cd(II)	49.47	33.4	30.67	29.9	35.55	30.31	26.4
Co(II)	44.82	40.68	35.43	30.1	40.6	33.8	29.09
Mg(II)	30.75	23.99	20.1	16.33	28.4	21.7	14.04
Al(III)	28.35	18.32	13.9	9.8	23.12	15.3	7.5
Pb(II)	15.15	10.55	7.42	1.8	10.2	6.81	2.5
Th(III)	15.09	10.07	6.5	3.2	13.9	9.63	3.1
Ni(II)	9.21	6.55	3.53	NS	7.32	5.3	NS
Ca(II)	7.14	3.68	NS	NS	5.16	3.23	NS
Zn(II)	5.73	2.77	NS	NS	3.07	NS	NS

NS: No observable sorption

Table 2 Binary separation of metal ions on POT CeI.

Separation achieved	Eluent	Metal ion (mg)		% Efficiency
		Loaded	Eluted	
Pb(II)	1M HNO ₃ + 0.1M NH ₄ NO ₃	2.00	1.96	98.00
Hg(II)	0.1M HNO ₃ +0.1M NH ₄ NO ₃	4.95	4.55	91.91
Ni(II)	0.1 M NH ₄ NO ₃	1.45	1.3	89.65
Hg(II)	0.1M HNO ₃ +0.1M NH ₄ NO ₃	4.5	4.23	94.00
Cd(II)	0.1 M NH ₄ NO ₃	1.20	1.13	94.16
Hg(II)	0.1 M HNO ₃ +0.1M NH ₄ NO ₃	4.32	4.15	96.06

Table 3 Quantitative removal of Hg(II) from wood industry effluents using column of POTCeI.

Sample	Metal Ion	Eluent used	In mg/100 mL
Wood industry wastewater (I)	Hg(II)	0.5 M HNO ₃	0.95
Wood industry wastewater (II)	Hg(II)	0.5 M HNO ₃	1.23

2,4,6-trinitrophenol Adsorption Studies

TNP was successfully removed from aqueous solution using POT CeI. The percentage of trinitrophenol that was adsorbed on the adsorbent (uptake %) was determined by comparing its concentrations before (C_i in ppm) and after (C_f in ppm) adsorption and can be calculated using the relation,²¹

$$\text{Uptake (\%)} = C_i - C_f / C_i \times 100$$

The concentration of TNP in the solution was determined by recording its absorbance using UV-Vis spectrophotometry at λ_{max} 355nm. Various factors like effect of contact time, pH of the solution, effect of temperature and influence of other metal ions on the adsorption of TNP by the nanocomposite exchanger were studied. For the study of all these factors, 50ppm of TNP solution and 0.1g of the exchanger dose was used throughout.

Effect of Contact Time

10mL of 50 ppm solution of TNP was shaken with 0.1 g of the exchanger for various time intervals at room temperature. 40% removal of TNP took place at the first two hours as the site for adsorption is vacant during the initial stage. The rate of adsorption then gradually decreased and reached the saturation after 6hours. After 6hours, about 75% of TNP was successfully removed from the solution using the exchanger (**Figure 2**). On further shaking, no appreciable adsorption was observed and hence 6hours was considered as the equilibrium time for further studies of other parameters.

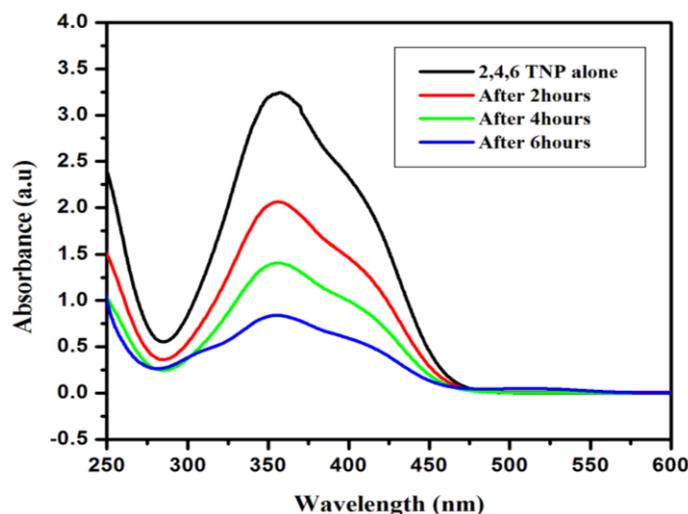


Figure 2 UV-Visible spectra of TNP showing effect of contact time on adsorption.

Effect of pH

The pH of the solution is an important parameter which determines adsorption capacity of the material. pH effect was studied by varying the pH from acidic to basic. 0.1 g of exchanger was shaken with 10mL of TNP solution from a pH ranging from 2 to 12 for 6 hours at room temperature. **Figure 3** shows that acidic pH ranging from pH 2 to 6 was not favourable for removal of TNP. This is because at lower pH more protons are available for competing with TNP solution for the active surface of the nanocomposite resulting in a repulsive interaction [22-23]. But at alkaline pH, the charge density of the solution is decreased and adsorption on to the surface of the material is favoured. About 73.4% of TNP adsorption was achieved at pH 12.

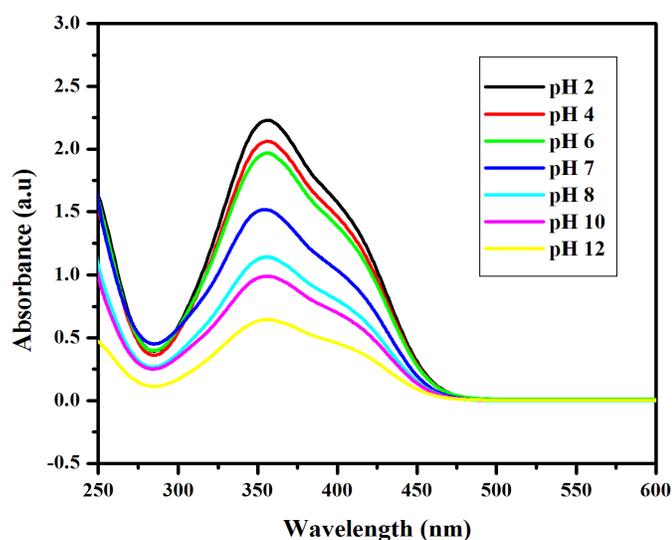


Figure 3 UV-Visible spectra of TNP showing effect of pH on adsorption.

Effect of Temperature

In order to study the effect of temperature on process of adsorption, the material was shaken with TNP solution at room temperature and at elevated temperatures at neutral pH for 6 hours. The results shows that as the temperature is increased, the rate of adsorption also increased, which may be because of the increased rate of diffusion of TNP molecules to the internal pores of the nanocomposite. 80% removal of TNP was attained at an elevated temperature of 50°C (**Figure 4**).

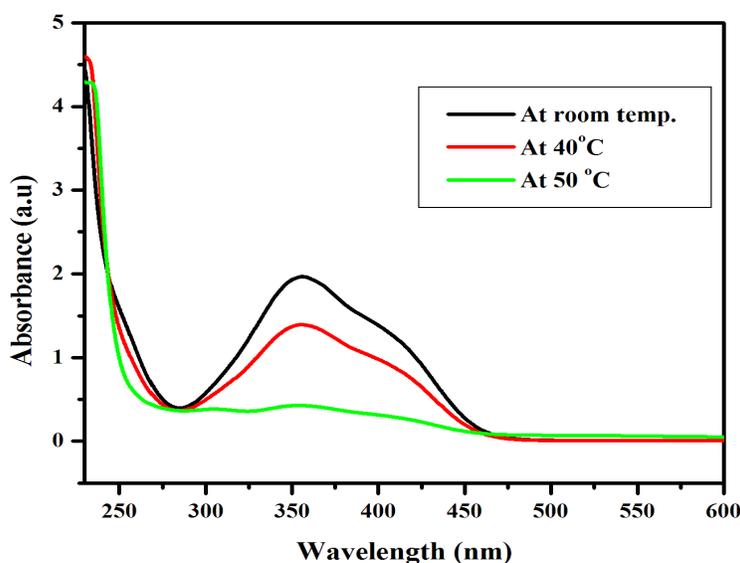


Figure 4 UV-Visible spectra of TNP showing the effect of temperature on adsorption.

From the data obtained, the optimum conditions were maintained to study the maximum removal capacity of the exchanger. For this, 0.1g of POT CeI was shaken with 50ppm 10 mL of TNP solution at pH 12 for 6hours, keeping the temperature at 50°C. Under these conditions, 95.36% removal was achieved.

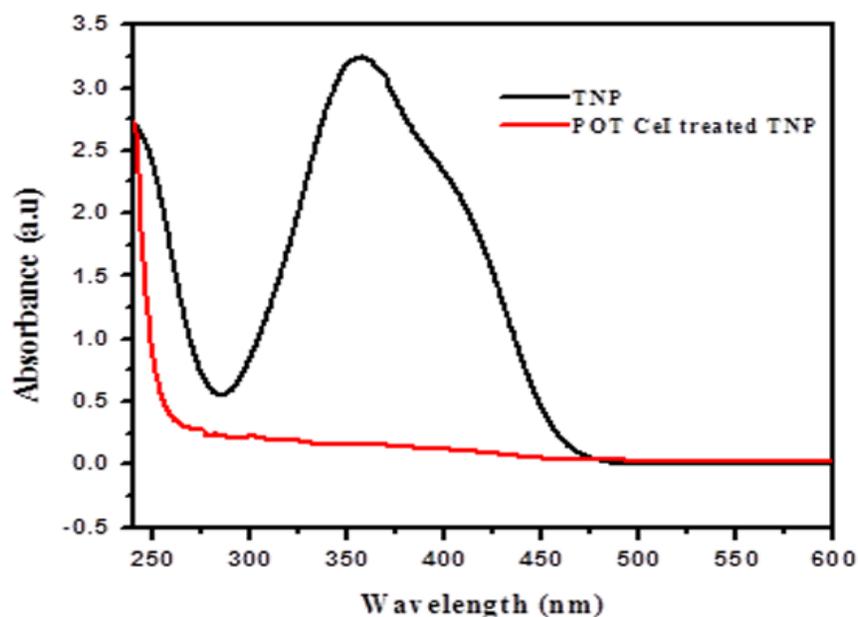


Figure 5 UV-Visible spectrum showing maximum removal of TNP under optimised conditions.

Effect of Other Metal Ions

As the discharge from industrial effluents also contains different heavy metal ions, the interference of other metal ions on adsorption is also an important factor to be studied. The effect of other metal ions like Hg(II), Cd(II), Co(II) and Cu(II) on adsorption were studied by adding 5mL of metal ion solution to 10mL of TNP solution and shaking it with 0.1g of exchanger for 6hours (**Figure 6**).

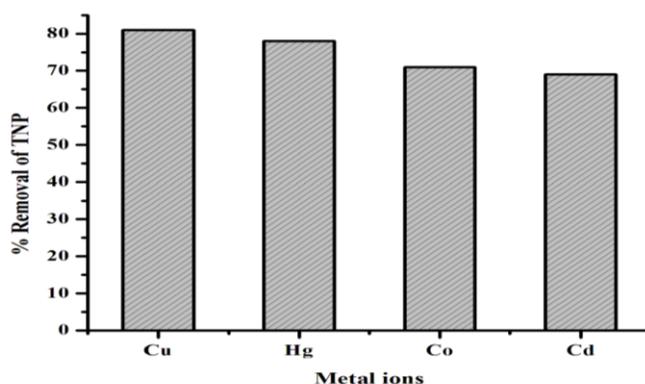


Figure 6 Influence of Cu(II), Hg(II), Co(II) and Cd(II) ions on adsorption of TNP.

It was observed that in presence of other metal ions the adsorption efficacy of the material is decreased. This is because in presence of other cations the active sites on the surface of the exchanger are blocked which results in the decreased affinity of TNP towards the exchanger.

Conclusion

The material POT CeI proved to be a successful candidate in the field of nanocomposite exchangers having the potential for removing about 95% of trinitrophenol from aqueous solution, which is a potent environmental pollutant. The effects of pH of solution, contact time, temperature and interference of other metal ions on adsorption of TNP were also investigated. The adsorption was favoured at higher pH and elevated temperature range. Besides the removal of TNP, the material showed good selectivity towards specific metal ions like Hg(II) and Bi(III), among which Hg(II) is a priority pollutant. Some important binary separations and quantitative removal of Hg(II) ions from industrial effluents were also carried out. The nanocomposite exchanger POT CeI can be used as an effective material for environmental remediation process.

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