Removal of toxic metal ions (Ni\(^{2+}\) and Cd\(^{2+}\)) from wastewater by using TOPO decorated iron oxide nanoparticles

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Abstract
In real engineering applications, nanoparticles can face hurdles of complex behavior of pollutants, for which electrostatic forces and background electrolyte can prove to be one of the robust mechanisms to remove pollutants from wastewater. In the present work, magnetite (Fe\(_3\)O\(_4\)) nanoparticles (NPs) and trioctyl phosphine oxide (TOPO) coated Fe\(_3\)O\(_4\) NPs were synthesized and characterized for removing divalent Ni\(^{2+}\) and Cd\(^{2+}\) ions. Morphological and chemical analysis of both NPs was performed, and batch adsorption experiments were performed to study the influence of different pH ranges, concentrations of adsorbents and different contact timings. TOPO functionalized magnetite nanoparticles were found to have better adsorption capacities as compared to Fe\(_3\)O\(_4\) at higher pH values. Isotherm models were run to identify the adsorption process. Langmuir isotherm model data fitted best for both metal ions adsorption, while Freundlich data suited best only for Ni\(^{2+}\) ions. The regression values for kinetic models confirmed that pseudo-second-order fitted best to the adsorption of both Ni\(^{2+}\) and Cd\(^{2+}\). Higher adsorption values were noticed for Ni\(^{2+}\) at higher dosages of both bare and TOPO-coated iron oxide NPs. Cadmium was found to have no influence of adsorbent dosage. Contact time was found to impact sorption values, i.e., adsorption was greater initially and then decreased with the passage of time. The study concludes that TOPO decorated Fe\(_3\)O\(_4\) NPs can be more efficiently used for wastewater treatment. Furthermore, the presence of alkyl chains in TOPO can be immobilized at surface of metals to undergo adsorption more efficiently.

Keywords  Trioctyl phosphine oxide (TOPO) · Adsorption · Heavy metals · Iron oxide · Wastewater · Isotherm · Kinetics · Batch reactions

Introduction
Water is one of the most crucial renewable resources for sustenance of all sorts of life, food and economic growth (Singh and Gupta 2016). In the present time, the need for water in anthropogenic work has risen up due to growing population. This increased urbanization and rapid fleet of industrialization are ultimately resulting in pollution of water and soil as indicated in Fig. 1, respectively (Vardhan et al. 2019). Anthropogenic activities like agriculture, industry, mining and smelting can result in gradual accumulation of heavy metals in the environment (Sardar et al. 2013). Heavy metal refers to the group metals and metalloids that have density greater than 4 ± 1 g/cm\(^3\) (Mohammed et al. 2011). However, more important than their density is their chemical properties that need serious attention in order to combat the threats they imply to all life forms. Heavy metals include lead (Pb), cadmium(Cd), zinc(Zn), mercury(Hg), silver(Ag), chromium(Cr) and copper(Cu)
and metalloids such as arsenic(As) (Duruibe et al. 2007). These metals can jeopardize human’s, microbe’s and plant’s life. They are recalcitrant to many biochemical reactions and thus difficult to remove. Even low concentrations of heavy metals can interfere with plant living system and may cause cancer in humans. They can produce ROS (reactive oxygen species) that suffocates underwater life (fishes and aquatic plants) (Singh and Kalamdhad 2011; Baragaño et al. 2020). Common methods for the removal of heavy metals include adsorption, ion exchange, filtration, biosorption, coagulation and cementation (Masindi and Muedi 2018) (Fig. 2).

In such a scenario, there is a need to introduce a system that would ensure robust elimination of heavy metals. Recently, nanoremediation has proved to be very effective for better adsorption efficiencies, low cost and durability of clean-up process as there is no need to pump ground water to surface site or transporting soil from one place to other (Rajendran and Sen 2018). Iron-based nanoparticles such

Fig. 1 Sources and consequences of heavy metals on all life forms (Srivastava et al. 2017; Jaishankar et al. 2014; Gheorghe et al. 2017)

Fig. 2 Typical structure of trioctyl phosphine oxide TOPO (Three octyl chains and one phosphine oxide group) [Chemical Book, TOPO 2017]
as nano-zero valent ion (nZVI) are found to be competing with most renowned techniques of in situ bioremediation and chemical reduction (Bardos 2015). Iron oxide nanoparticles due to their infinite surface area and accurate sizes can result in greater degree of adsorption to various heavy metals says Al-Saad et al. (2012).

Iron oxide nanoparticles are selected as they offer a number of advantages including their inert and non-toxic thus making it easier to apply their magnetic properties in environmental regimes. Their abundant occurrence in earth makes it feasible and cost-effective approach to use. Targeting of site-specific contaminated zone through magnetic support is another advantage. Moreover, the process of adsorption occurs on external surface of iron oxide thus ensuring less adsorption time (more kinetic rates). Iron oxide has high surface-to-volume ratio thus providing more active sites for the heavy metal to attach. Moreover, it becomes easier to separate the adsorbate liquid by magnetic force. Iron oxide nanoparticles are reusable. They are highly dispersed in liquid system thus not involving the problems of membrane fouling, high-pressure treatment and packed column plugging (Nassar 2012).

Surface functionalization is the very first requirement for the real applicability of iron oxide nanoparticles. Thus promising extended stability and withstanding harsh conditions of pH and electrolyte. The famous Derjaguin–Landau–Verwey–Overbeek (DLVO) theory is used to find out the interaction capacity around the surface of a particle. The colloidal stability of nanoparticles is assigned to the balance between repulsive and attractive forces. For iron oxide nanoparticles, these attractive forces are due to Van der Waal forces and magnetic forces of nanoparticles acting as magnetic dipoles (Walter et al. 2015).

In order to control the aggregation and interactions of bare iron oxide nanoparticles, they are often treated with surfactants such as TOPO (Triocyl phosphate oxide). TOPO (properties briefly given in Table 1) is an organophosphorus compound and a white crystalline solid used as stabilizing agent for a variety of nanoparticles (Chemical Book, TOPO 2017). TOPO was considered as an attention-grabbing laboratory compound since 1970’s when for the first time it was used at Oak Ridge National Laboratory scientists recovered uranium from the wet process phosphoric acid. Apart from this TOPO was used for recovery of organics from fermentation broth (Watson and Rickelton 1992).

In the present study, magnetite nanoparticles conjugated to TOPO were used as an adsorbent system to remove cadmium and nickel heavy metals from synthetic wastewater solutions. Magnetite nanoparticles due to their abundant nature and high capacity for adsorbing heavy metals can be used along with TOPO as stabilizing agent that proves to be one of the efficient removal systems so far in nanoremediation.

### Methods

#### Materials

Ferrous sulphate hepta hydrate $\text{FeSO}_4\cdot7\text{H}_2\text{O}$ (Molecular weight: 278.02 g/mol), Sodium borohydride $\text{NaBH}_4$ (Molecular weight: 37.83 g/mol), n-Hexane, Triocylphosphine oxide (TOPO) (Molecular weight:386.6 g/mol), Cadmium nitrate $\text{Cd(NO}_3)\cdot4\text{H}_2\text{O}$ (Molecular weight:308.48 g/mol), Nickel (II) Chloride $\text{NiCl}_2\cdot6\text{H}_2\text{O}$ (Molecular weight:237.73 g/mol).

#### Experiment

**Surface functionalization of iron oxide nanoparticles with triocylphosphine oxide (TOPO)**

5 Mm TOPO (Triocylphosphine oxide) was prepared in a 100 ml flask containing 25 ml hexane. 2.5 g of iron salt (Ferrous sulphate) was added to 200 ml distilled water and stirred for 30 min to prepare a true solution. TOPO solution was then added to the iron salt solution and stirred for 1 h at maximum speed. Following this, the above solution was then added to ice cold $\text{NaBH}_4$ (1%). Color change was observed from yellow to blackish brown. Purification of pellets was undergone through centrifugation at 10,000 rpm for 10 min and washed three times with distilled water. The pellets were then dried in a drying oven at 50 °C for 2 days. Afterward, the TOPO bound iron oxide nanoparticles were scratched and powdered through pestle and mortar to make a fine powder which was then subjected to characterization.

**Preparation of artificial waste water**

Artificial water samples were prepared by mixing standard heavy metal solutions of cadmium nitrate $\text{Cd(NO}_3)\cdot4\text{H}_2\text{O}$ and nickel chloride $\text{NiCl}_2\cdot6\text{H}_2\text{O}$ salt solutions. Stock solutions of these heavy metal solutions were prepared by mixing 10 mg of both the salts to 1000 ml distilled water.

**Batch adsorption experiments**

Batch adsorption experiments were performed in the laboratory of Nano biotechnology lab of Quaid-i-Azam University, Islamabad, Pakistan. The aim of the present work was to explore as how increase or decrease in pH can affect the adsorption phenomena of the divalent ions on the surface of magnetite NPs and TOPO bound magnetite NPs. Stock solutions of salts cadmium nitrate and nickel chloride 10 mg each separately mixed in 1000 ml distilled water out of which sets of experiments were performed for elucidating the effect of different pH (5, 6, 7, 8) at different time intervals using a pH meter equipped with electrodes. 1 M sodium hydroxide NaOH.
Langmuir isotherm Theoretical model developed by Irving Langmuir in 1916 is the most widely employed isotherm model for adsorption studies. Basic concept of this model is the monolayer coverage of the adsorbate on homogenous surface. This model assumes that all sites of adsorbent are homogenous and the forces of interaction are minor. Therefore, once the adsorption takes place and occupied by molecules in all respective (homogenous) sites of the adsorbent, then further no adsorption occurs (Chowdhury et al. 2011; Terdputtakun et al. 2017).

Linear equation for Langmuir model is written as \( 1/q_e = 1/Q_m + 1/bQ_m + 1/C_e \)

With the help of Microsoft Excel 2010, linear graphs were constructed as \( C_e/q_e \) versus \( C_e \).

\( Q_m \) value was calculated from the formula \( Q_m = Q_m - b.C_e \). This \( Q_m \) is actually the least sorption capacity of adsorbent (on peak time interval) at equilibrium (after which desorption starts). The linear graph will produce \( y = mx + c \). Where \( m \) is the intercept equal to \( 1/b.Q_m \) and slope = \( 1/Q_m \).

Freundlich isotherm In the presence of multiple layers or sites available for adsorption, the Langmuir model is unable to explain the adsorption phenomena, and therefore, Freundlich isotherm model is applied to explain heterogeneous adsorption behavior on the surface of adsorbent. In 1909, Freundlich explained the first mathematical model to a non-linear isotherm resulting into a pure empirical formula for adsorption on heterogeneous sites (Rahbaralam et al. 2020).

Equation for Freundlich isotherm is written as \( \log q_e = \log Kf + 1/n \log C_e \)

From the above equation, Freundlich plots were constructed as \( \log q_e \) against \( \log C_e \).

\( Q_e \) value was calculated via the formula \( Q_e = Kf.Ce^{1/n} \). Slope = \( 1/Q_m \) and Intercept = \( 1/b \).Qm.

Pseudo-first-order kinetics Equation for pseudo-second-order kinetic model is given as

\( \log (q_e - q_i) = \log (q_e) - (k1/2.303)t \)

Plot constructed as \( \log (q_e - q_i) \) versus time\( t \). This gives a slope equal to \(-k/2.303\) and an intercept equal to \( \log (q_e) \).

Pseudo-second-order kinetic Equation for pseudo-second-order kinetic model is written as

\( t/q_t = 1/k2q_e^2 + (1/q_e)t \)
$k_1$ (1/min) and $k_2$ (g/mg min) are the pseudo-first-order and second-order rate constant.

The linear plots of pseudo-first-order and pseudo-second-order kinetics were used to calculate the values of kinetic parameters.

$q_t$ is amount of cadmium ion and nickel ion on the surface of iron oxide and TOPO Functionalized iron oxide NPs at any time, $t$, (mg/g). $h$ is the initial sorption rate. ($h = q_t/t$) when $t$ approaches 0, then $h$ (mg/g min) becomes $kq_e^2$. Values of $k$ and $h$ are determined from slope and intercept as $k = \text{slope}^2/\text{intercept}$ and $h = 1/\text{intercept}$.

Regression analysis

In the present study, linear regression analysis was done to determine the values of isotherm and kinetic model parameters. The values of correlation coefficient ($R^2$) were obtained from the graphs generated by using Microsoft Excel 2010. Through this value, it was studied which isotherm or kinetic model best fits the data. Higher the values of $R^2$, more appropriate the data are value of regression coefficient that may vary from 0 to 1 (Sogut and Caliskan 2017). $R^2$ values were generated through the following Eq. (6) (Chen 2015).

$$R^2 = \frac{(q_m - \bar{q}_e)^2}{(q_m - q_e)^2 + (q_m - \bar{q}_e)^2}$$

where $q_e$ is the equilibrium capacity obtained from experiments, $q_m$ is the constant obtained from isotherm model, and $\bar{q}_e$ is the average of $q_e$, respectively.

Results and discussion

Characterization of adsorbents

XRD study

Crystal structure and average diameter of nanoparticles were analyzed through X-ray diffraction. XRD patterns of each sample are shown Fig. 3. Characteristic diffraction peaks of the iron oxide nanoparticles are 30.12, 35.59, 43.15, 57.25 and 62.45 which, respectively, corresponds to (220), (311), (400), (511) and (440) planes of magnetite nanoparticles. Same results were found in work of (Mazrouaa et al. 2019). Also, these XRD peaks are in accordance with the (JCPDS 19-629). The TOPO functionalized iron oxide nanoparticles are showing their respective peaks on 30.12, 35.69, 43.84 and 62.17 (at 20 degrees) which coincide with hkl plane of cubic magnetite as 220, 311, 400 and 400 respectively, obtained from its JCPDS Card No.19-0629 (Rusianto et al. 2015).

FTIR study

The characteristic peaks of Fe–O bonding in iron oxide sample are found at ranges of 579 cm$^{-1}$. For nanoparticles to be magnetite in nature, they need to display FTIR peak at 580 cm$^{-1}$ (Petcharoen and Sirivat 2012). Absorption band at 3354 cm$^{-1}$ might be due to the moisture content absorbed by the nanoparticles from atmosphere. Bands at 1320–1000 indicate C–O stretches (Fig. 4a). The peaks corresponding to TOPO functionalized nanoparticles were found around at 996 cm$^{-1}$ range for the presence of phosphine oxide functional group i.e., being found in TOPO molecule. Same results were reported by (Xu et al. 2011). Another study done by Zhang et al. (2012) confirms that the peaks around 990–1300 cm$^{-1}$ confirm the attachment of functional group P = 0 in TOPO. Peaks around 579 cm$^{-1}$ range are characteristic of Fe–O bond in magnetite nanoparticles. Bands at 3165 cm$^{-1}$ might be due to the terminal alkyl groups; C–H stretches (Fig. 4b). A similar study says that for TOPO functionalized iron oxide additional peaks at around 2926 cm$^{-1}$ confirm the attachment of TOPO (Batra and Datta 2019).

SEM study

Morphological studies of samples were done using high-resolution scanning electron microscopy. Sample of iron oxide presented a large number of dispersive cubic structured nanoparticles. SEM micrographs are presented in Fig. 5 where the TOPO functionalized nanoparticles...
displayed cubic spinel structures with efficient attachment of white crystalline trioctyl phosphine oxide. Thus, the SEM images of iron oxide NPs confirm that they are in nanoscale range and trioctyl phosphine oxide is effectively conjugated to iron oxide NPs. Same results were found in the work of Alatorre et al. (2019). They employed non-conventional chemical method using external magnetic field to synthesize iron oxide nanoparticles. Same SEM images were found in a study by Lim et al. (2014) who used ferrous sulphate and ferrous nitrate as salt precursors in the presence of NaOH to synthesize iron oxide nanoparticles. In another study, Li et al. (2017) generated cube-like nanoparticles by two-stage oxidation method and sphere like by single-stage oxidation method.
Adsorption isotherms

Fitting of adsorption isotherms equation to experimental data is the most crucial step in data analysis (Kinniburgh 1986). Adsorption isotherm is an empirical relationship employed to analyze the amount of solute (adsorbate) adsorbed on adsorbent. Adsorption isotherm is a graph that reveals the relationship between amount adsorbed by a unit gram of sorbent and the amount of metal ions left in an experimental medium after equilibrium along with distribution of metal ions between solid and liquid phases (Desta 2013). Among isotherm models, Langmuir and Freundlich adsorption isotherms models are the most widely studied. The Langmuir model is associated with monolayer coverage onto the adsorption sites, whereas Freundlich isotherm is associated with reversible adsorption and explains heterogeneous surface of adsorption (Khajavian et al. 2019). In the present study, Langmuir and Freundlich isotherm models were applied to find equilibrium ($Q_e$) between heavy metals cadmium and nickel on iron oxide nanoparticles (IONPs) and TOPO functionalized nanoparticles (TF IONPs) and the ion’s concentration ($C_e$) at constant temperature. Linearized form of Langmuir and Freundlich isotherms is stated in Eqs. (9) and (11) (Table 1).

### Table 1 Chemical properties of TOPO. Retrieved from National library of Medicine, [PubChem], [Chemical Book, TOPO 2017]

| Name of features          | Description                                      |
|---------------------------|--------------------------------------------------|
| Molecular formula         | C24H51OP                                         |
| IUPAC Name                | 1-dioctylphosphoryloctane                        |
| Exact Molecular mass      | 386.367753 g/mol                                  |
| Topological surface area  | 17.1Å²                                            |
| Form                      | White/yellow crystalline powder                  |
| Density                   | 0.88 g/cm³                                       |
| Melting point             | 50–52 °C                                          |
| Boiling point             | 201–202 °C                                       |
| Solubility                | Less than 1 g/L                                  |

#### Langmuir isotherm

The Langmuir isotherm model assumes the formation of monolayer of metal molecules on the outer surface of adsorbent after which no further adsorption takes place on adsorbent surface. It explains the equilibrium distribution of metal ions between liquid and solid phases (Dada et al. 2012). Mathematically, the equation is given as
where \( q_e \) is solute (adsorbate) uptake per unit weight of iron oxide and functionalized iron oxide nanoparticles (mg/g)

\[
q_e = \frac{b Q_m C_e}{1 + b C_e}
\]

Linearized form:

\[
\frac{C_e}{q_e} = \left( \frac{C_e}{Q_m} \right) + \frac{1}{b Q_m}
\]

at equilibrium solute concentrations, \( C_e \) is the equilibrium concentration of adsorbate in solution (mg/L), and \( Q_m \) and \( b \) are Langmuir constants associated with the sorption capacity and energy of adsorption, respectively. The plots of \( C_e/q_e \) versus \( C_e \) show that adsorption of Ni\(^{2+}\) and Cd\(^{2+}\) gives a straight line which is represented in (Fig. 6a–d).

Values of \( Q_m \) and \( b \) of the linear equation of Langmuir adsorption isotherm were derived from the slopes and intercepts of the

![Fig. 6 Langmuir isotherm plots for adsorption of (a) magnetite NPs (2 mg/20 ml) to Cd at pH8, (b) TOPO coated magnetite NPs (2 mg/20 ml) to Ni at pH8, (c) magnetite NPs (2 mg/20 ml) to Cd at pH5 (d) TOPO coated magnetite NPs to Cd at pH 6](image)

### Table 2 Parameters of isotherm adsorption models for adsorption of nickel metal ions on iron oxide and TOPO functionalized iron oxide nanoparticles at 25 °C and different pH ranges, i.e., 5, 6, 7, and 8

| pH range | Langmuir parameters | Freundlich parameters |
|----------|---------------------|-----------------------|
|          | \( R^2 \) | \( Q_m \) | \( b \) | \( Q \) | \( R^2 \) | \( K_f \) |
| For FeO 2 mg/20 ml nickel metal ion | \[ pH5 \] 0.9527 0.006394271 0.832304417 0.747216618 0.9987 0.51315184 | 51.1315184 |
| FeO 4 mg/40 ml | \[ pH6 \] 0.9965 0.003153977 0.400991539 0.90821508 0.9978 9.21645273 | 2.91645273 |
| For FeO 2 mg/20 ml | \[ pH7 \] 0.9664 1.669727834 0.438371115 0.356544372 0.9883 1.497783827 | 1.497783827 |
| For FeO TOPO 2 mg/20 ml | \[ pH8 \] 0.9995 0.058102376 0.524757607 0.611845326 0.9998 3.21535649 | 3.21535649 |
| For FeO TOPO 4 mg/40 ml | \[ pH6 \] 0.5655 0.315000315 0.485093899 0.233198078 0.9646 1.882870306 | 1.882870306 |
| For FeO 4 mg/40 ml | \[ pH5 \] 0.8912 0.018933298 0.947844907 0.044901441 0.9698 33.3749395 | 33.3749395 |
| For FeO 2 mg/20 ml | \[ pH6 \] 0.9963 0.880492823 0.478704133 0.187286961 0.9987 1.859705339 | 1.859705339 |
| For FeO TOPO 2 mg/20 ml | \[ pH7 \] 0.9949 0.326541275 0.815791577 0.16677507 0.9995 3.939618922 | 3.939618922 |
| For FeO TOPO 4 mg/40 ml | \[ pH8 \] 0.9993 3.8925652 1.162443439 0.444385193 1 1.704514468 | 1.704514468 |
| pH6 | 0.5899 4.723665564 0.501539919 0.449357419 0.7501 1.029277092 | 1.029277092 |
linear plots of $C_e$ versus $C_e/q_e$ in (Fig. 6a–d). Values of $q_m$ and $b$ are represented in Tables 2 and 3, respectively. The isotherm was found to be linear in most of the concentration ranges studied displaying with best linear correlation values $R^2 = 0.9995$ and 0.9993 for nickel when adsorbed to IONPs and TF IONPs, respectively. Whereas correlation values were $R^2 = 0.9983$ and 0.9818 for cadmium adsorption to IONPs and TF IONPs. Thus, confirming the monolayer coverage of cadmium and nickel (pollutants) on the applied sorbents, i.e., IONPs and TF IONPs respectively.

Freundlich isotherm

While Langmuir isotherm says that enthalpy of adsorption does not depend on concentration of metal ions adsorbed, the empirical Freundlich isotherm equation which is based on adsorption on heterogeneous sites can be derived by supposing a logarithmic decrease in the enthalpy of adsorption with the increase in the number of adsorption sites (Meroufel et al. 2013). The Freundlich isotherm suggests adsorption phenomena to occur on heterogeneous surfaces (Ayawei et al. 2017). Mathematical form of Freundlich equation is given as:

$$q_e = K_f C_e (1/n)$$

(10)

Linearized form :

$$\log q_e = \log K_f + (1/n) \log C_e$$

(11)

where $K_f$ is adsorption capacity (L/mg), and $1/n$ is adsorption intensity. It also indicates relative distribution of energy and the heterogeneity of adsorbates. Both $K_f$ and $1/n$ are Freundlich constants. These are calculated from the slope and intercept of graph log$q_e$ vs. log$C_e$ which are shown in Fig. 7a–d, respectively. The parameters for Freundlich model are jotted down in Tables 2 and 3, respectively. Comparing the results of regression coefficient values for nickel and cadmium, we can find best $R^2$ values for nickel equal to 1 in case of TOPO functionalized iron oxide showing that Freundlich isotherm fitted best for the experimental data in case of nickel adsorption (Zhang et al. 2020). On the other hand, best $R^2$ values of cadmium are found to be 0.998 for adsorption on IONPs and 0.992 for adsorption on TF IONPs. Overall we can find that $R^2$ values of Freundlich model for both the metals are best as compared to Langmuir model which reveals that the data best fits for Freundlich model. This explains the process of adsorptions to occur at heterogeneous sites on both the adsorbents IONPs and TF IONPs respectively.

**Adsorption kinetics**

Kinetic models help to access the time of stock piling of heavy metals on the surface of adsorbent consequently aiding in revealing the rate of adsorption (Samad et al. 2020). Chemical kinetics are very important to know about the rate constants of reaction and to determine whether the adsorption process takes place quickly or slowly (Adane et al. 2015). In order to conduct the kinetic study of nickel and cadmium removal by IONPs and TF IONPs, experimental data were used for pseudo-first-order and pseudo-second-order kinetic model. Overall the rate of cadmium and nickel adsorption was relatively higher in early stages but gradually decreased over time when equilibrium was achieved. This can be due to the high availability of active sites in initial stages and gradually over time these active sites get packed.
with nickel and cadmium creating lower number of active sites for further adsorption due to which the rate of adsorption decreases (Duarte Neto et al. 2018).

**Pseudo-first-order kinetics (Langergren’s)**

Pseudo-first-order kinetic model was applied to study the rate of adsorption of nickel and cadmium ion on IONPs and TF IONPs at equilibrium or at any time. Pseudo-first-order kinetics undergoes physisorption process (Gusain et al. 2019) and is represented mathematically in Eq. (12).

\[
\log\left( q_e - q_t \right) = \log(-K_1 t/2.303)
\]

(12)

where \( q_e \) and \( q_t \) are amounts of adsorbates (mg/g) at equilibrium, and time \( t \) (s) \( K_1 \) is the rate constant of pseudo-first-order kinetics. The plot \( \log (q_e - q_t) \) versus time \( (t) \) gives a straight line that finds \( K_1 \) and \( q_e \) from slope and intercept. The respective plots for pseudo-first-order are shown in Fig. 8a–d. Values of \( K_1 \) and regression coefficient are jotted down in Tables 4 and 5 for nickel and cadmium adsorption by the two types of adsorbents. Comparing the values of regression coefficient, we get best values of \( R^2 \) at higher adsorbent doses (4 mg/40 ml) of IONPs equal to 0.935 at pH 6 for nickel adsorption, and for TF IONP (4 mg/40 ml) sample, we get \( R^2 \) value equal to 0.932 at pH 6. Whereas for cadmium metal adsorption, the \( R^2 \) value was found to be 0.943 at 2 mg/20 ml at pH 8 when adsorbed to IONPs sample and \( R^2 \) value was 0.9708 for TF IONPs (2 mg/20 ml concentration) at pH5. These values indicate that at such pH values and concentration of adsorbent, the process of kinetic adsorption favors physisorption phenomena.

**Pseudo-second-order model**

Pseudo-second-order kinetics follows chemisorption process. Linearized form of pseudo-second-order kinetics is given in Eq. (13)

\[
t/q_t = 1/K_2 q_e^2 + 1/q_e
\]

(13)

where \( K_2 \) is the rate constant for pseudo-second-order model mg/g per minute. Value of \( K_2 \) depends on experimental conditions such as initial pH and solution agitation rate, temperature and concentration. The value of \( k2 \) lowers with increasing concentration of solution as it takes longer time to attain the equilibrium (Aly et al. 2014).

Pseudo-second-order plots \( t/q_t \) versus time (min) gave a straight line as indicated in Fig. 8e, f. The values of \( k2 \), \( q_e \) and \( R^2 \) are calculated from the plots and jotted down in Tables 4 and 5, respectively. The linear correlation coefficient values are higher, i.e., 0.98 for sample TF IONPs (2 mg/20 ml) at pH 6 for adsorption nickel and 0.96 for IONPs (2 mg/20 ml) sample at pH5 for cadmium metal adsorption.
adsorption. Additionally, the values of $q_e$ (cal), i.e., calculated adsorption capacity were not in close agreement with the experimental adsorption capacity, revealing that removal of metal ions by adsorbent followed pseudo-second-order. The data suggest the chemisorption process, and it might be due to the exchange of metal ions with the functional groups of iron oxide NPs and TOPO functionalized iron oxide NPs (Cheng et al. 2020).

**Effect of different parameters on adsorption of metal ions onto sorbent surface**

The results generated overall from isotherm and kinetic models give us a clear indication that while working with IONPs and TF IONPs one can clearly observe fluctuations in adsorption capacities as being directly influenced by different values of pH, i.e., different conditions of acidic and basic environments. Apart from this effect of adsorbent dose and contact time was also studied that was found to have a notable influence upon the adsorption capacity.

**Effect of pH**

pH value is one of the most crucial factors that governs the binding of heavy metal ions on the surface of adsorbents since the hydrogen ions concentration has the direct consequence on the adsorption sites of the adsorbent (Ouyang et al. 2019). The effect of pH on the removal of Ni$^{2+}$ and Cd$^{2+}$ through IONPs and TF IONPs was studied by adjusting the pH in the range of 5–8 by adding 0.1 M HCl and
0.1 M NaOH to the metal ion solutions. The present study showed that the removal of cadmium and nickel ion was highly dependent on pH conditions. Results from Langmuir data showed that the amounts of Ni cation concentrations adsorbed to iron oxide were found to be lesser at lower pH values. Good adsorbability was obtained in the case of TF IONPs adsorbent. The steady values achieved for TOPO functionalized nanoadsorbents were 1.1 mg/g at pH 5, 2.7 mg/g at pH 6, 2.2 at pH 7, and 14 mg/g at pH 8. This can be explained by the fact that the Ni^{2+} ions start to compete with active sites of adsorbent at lower pH. With increased pH as for in the case of TOPO functionalization, the P=O groups become free due to undoping thus resulting in efficient removal of Ni^{2+} ions. Less adsorption of nickel in strong acidic or basic conditions might be due to the presence of electrostatic interactions created due to Ni (OH)_{3}^{−} and Ni(OH)^{+} ions in the solution (Muhammad et al. 2020). On the other hand, Langmuir data for cadmium show that the adsorption capacities were found to be higher even at low pH ranges, i.e., q_e values were 8.0 mg/g at pH 5 and 3.5 mg/g at pH 8. This is due to the fact that oxygen-containing functional groups on the surface of adsorbent gets ionized hence aiding in adsorption (Sitko et al. 2013).

### Effect of contact time

Contact time was maintained at 0–50 min for samples recorded at pH 5, 6, 7 and 8 with 2 mg/ml concentration of both the adsorbents and 0–100 min for samples recorded at pH 6 with 4 mg/ml of adsorbent concentration.

### Table 4

| pH range | Pseudo-first-order parameters | Pseudo-second-order parameters |
|----------|-------------------------------|-------------------------------|
|          |                  |                               |
| For FeO 2 mg/20 ml nickel metal ion |
| pH5      | 0.6361 0.0778626 1.871607711 | 0.005131424 0.017974943 0.0051 |
| pH6      | 0.8859 0.2436574 6.26566416   | 0.000797035 0.043092304 0.0028 |
| pH7      | 0.7735 0.0693203 8.787346221  | 0.036024377 2.781641168 0.8055 |
| pH8      | 0.8039 0.3712436 3.249918752  | 0.032067499 0.33869602 0.2398 |

### Table 5

| pH range | Pseudo-first-order parameters | Pseudo-second-order parameters |
|----------|-------------------------------|-------------------------------|
|          |                  |                               |
| For FeO 2 mg/20 ml cadmium metal ion |
| pH5      | 0.0952 0.1524586 0.236423387 | 0.005131424 0.017974943 0.0051 |
| pH6      | 0.8355 0.0449085 0.069749599 | 0.005131424 0.017974943 0.0051 |
| pH7      | 0.6229 0.0262542 1.337971635 | 0.005131424 0.017974943 0.0051 |
| pH8      | 0.9437 0.0603386 0.87627059  | 0.005131424 0.017974943 0.0051 |

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This content is from a scientific journal article and is intended for educational and research purposes. It should not be used for any other purpose. Any use of this content beyond the limitations set forth in the applicable terms of use constitutes an infringement of the rights of the owner and of the author.
The adsorption capacities on the proposed time intervals showed that values of $q_e$ were greater initially, and then, with the lapse of time, the adsorption decreased. This can be explained due to the fact that as the time increases the number of available active sites of adsorbents gets occupied by the heavy metal ions resulting in saturation of sorbent surface and decreasing the pore diffusion of the ions (Kahrizi et al. 2018; Hosseini et al. 2019).

**Effect of adsorbent dose**

The adsorbent dose was set at two concentrations which were 2 mg/ml and 4 mg/ml doses of adsorbent at pH 6. The results showed that adsorbent dose has an impact on the Qm values in case of nickel metal adsorption. The $Q_m$ values were recorded to be lesser, i.e., 0.0031 at 2 mg dose of adsorbent (IONP) and greater, i.e., 0.315 at 4 mg adsorbent (IONP) dose. For TOPO functionalized adsorbent sample, the $Q_m$ value was found to be 0.8 at 2 mg dose and quite greater, i.e., 4.7 at 4 mg/ml of adsorbent dose. As the adsorbent dosage increases, the number of available active sites tends to be greater thus providing greater number of sites for the metal ions to attach. (Phuengprasop et al. 2011). In case of cadmium adsorption, the adsorbent dose was found to have no impact on adsorption efficiency. This might be due to the electrostatic repulsions between the metal cations possibly causing hindrance in the adsorption of metal ions (Razaq et al. 2020). While determining the effect of dose other variables (pH 5, 7, 8), and contact time was kept constant.

**Conclusion**

Iron oxide nanoparticles are research suitable nanoparticles that are found to be most useful in removing heavy metal contaminants due to their magnetic properties. Trioctyl phosphine oxide on the other hand is used a surface functionalization agent and a good extractant for the recovery of radioactive waste such as uranium metal. The present study was aimed keeping in front the magnetic properties of Fe$_3$O$_4$ NPs and extractant ability of TOPO to remove heavy metals such as Ni$^{2+}$ and Cd$^{2+}$ cations in synthetic wastewater. The two adsorbents Fe$_3$O$_4$ NPs and TOPO bound Fe3O4 NPs were tested for their adsorption capacities by providing different pH conditions such as at pH 5, 6, 7 and 8. It was found that Fe3O4 NP’s and TOPO bound Fe3O4 NPs shows better adsorption capacities at basic conditions, i.e., equilibrium adsorption values were 14 mg/g for both the adsorbents in case of nickel cations. This is because at higher pH values, the functional groups of adsorbents get free resulting in efficient attachment to heavy metal ions thus giving higher adsorption values. The adsorption capacities of the relevant time intervals showed that values of $q_e$ were greater initially and then decreases gradually because of the fact that when time increases the number of available active sites of adsorbents gets occupied by the heavy metal ions resulting in saturation of sorbent surface and decreasing the pore diffusion of the ions. Higher adsorption values were observed for Ni$^{2+}$ adsorption at higher concentrations of both bare and TOPO coated Fe$_3$O$_4$ NPs. The $R^2$ values of Freundlich isotherm model were higher as compared to Langmuir model which shows the data best fitted to Freundlich isotherm which indicates that the process of adsorption occurs at heterogeneous sites on the surface of Fe$_3$O$_4$ NPs and TOPO bound Fe$_3$O$_4$ NPs. On the other hand, the $R^2$ values for Cd$^{2+}$ and Ni$^{2+}$ showed the data best fitted to pseudo-second-order model. Finally, it can be concluded that TOPO functionalization of Fe$_3$O$_4$ NPs proves to be a satisfactory approach in remediating contaminants from wastewater.

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**Declarations**

**Conflict of interest** Authors declare no competing interest and affirm that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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