



# Synthesis of phosphorylated raw sawdust for the removal of toxic metal ions from aqueous medium: Adsorption mechanism for clean approach

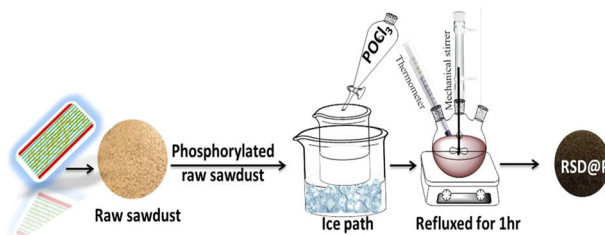
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## Abstract

In this work, phosphorus oxychloride was grafted onto the surface of raw sawdust (RSD) particles to get effective adsorbent for capturing Cd(II), Cr(III), and Pb(II) metal ions from aqueous medium. Phosphorylated raw sawdust (RSD@P) was characterized by FTIR, TGA, SEM-EDX, TEM, BET, and XPS analyses. Various experimental conditions of adsorption viz. pH, contact time, temperature, and initial concentration were optimized. The adsorption behavior of RSD@P concerning adsorption kinetics, isotherms and thermodynamics was also studied. The values of  $q_e$  for Cd(II), Cr(III), and Pb(II) metal ions onto RSD@P was found to be 244.3, 325, and 217 mg/g, respectively at 298 K according to monolayer Langmuir adsorption. The adsorption kinetics data revealed that Cd(II), Cr(III), and Pb(II) metal ions were well fitted to pseudo-second-order kinetic model. The thermodynamic results demonstrated that adsorption was spontaneous and exothermic. The mechanisms of interactions was also discussed for the adsorption of Cd(II), Cr(III), and Pb(II) metal ions over RSD@P. The obtained results showed that RSD@P was an auspicious adsorbent which showed outstanding reusability for the removal of metal ions from aqueous medium.

## Graphical Abstract



**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s10971-018-4870-0>) contains supplementary material, which is available to authorized users.

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## Highlights

- Crosslinked phosphorylated raw sawdust (RSD@P) was prepared.
- The material (RSD@P) was used for the removal of Cd(II), Cr(III), and Pb(II) from aqueous medium.
- Adsorption of all metal ions onto RSD@P was rapid, spontaneous, and exothermic.
- The values of  $q_e$  for Cd(II), Cr(III), and Pb(II) was 244.3, 325, and 217 mg/g, respectively.
- The RSD@P was regenerated by simply washing with 0.1 M HCl solution.

**Keywords** Phosphorylated sawdust · Adsorption · Toxic metals · Adsorption models

## 1 Introduction

Obtaining pure water is a major concern and great demand for humane life because it is continuously polluted by toxic heavy metals which leads to serious environmental problems to many forms of life [1–3]. Aqueous wastes of many industries, modern urbanization, mining and dissolution from the associated geologic formations are main sources of water contamination by heavy metals [4, 5]. Lead, cadmium and chromium are main metals whose existence in aqueous solutions leads to many health problems [6–8]. So, it is one of the most important challenges to the scientist to remove these toxic metal ions from aqueous environment [9, 10]. Several trials and efforts have been demonstrated using various treatments such as adsorption, ion exchange, reverse osmosis, chemical precipitation, electrochemical removal, and biosorption [11–14].

Adsorption has considerably been used because of its effectiveness and economic visibility. Lead, cadmium, and chromium has been removed by using several adsorbents [7, 15–17]. In recent years, the search for economical and convenient adsorbents based on naturally found materials and/or their modification has been increasingly demanded. Sawdust, as one of the alternative absorbent materials has been particularly used for the exclusion of various metal ions from aqueous medium [5, 18, 19]. Wood sawdust is widely available as a waste of carpenter workshops and its chemical composition contains cellulose, hemicelluloses, and lignin. Hence, we attempted to modify the wood sawdust to increase its efficiency for heavy metal removal. The modification process was based on increasing the uptake capacity through introducing phosphate as ion exchange groups. Recently, the oak tree sawdust has been modified by phosphate groups using phosphoric acid for the removal of lead ions [20]. However, our modification involves a new procedure for phosphorylation the hydroxyl groups on wood sawdust components using phosphorous oxychloride. The modified sawdust was subjected to different analyses and its applications for the adsorptive removal of lead, cadmium and chromium was also examined.

## 2 Experimental

### 2.1 Materials and chemicals

The chemicals and reagents which were used here were of analytical reagent grade. HNO<sub>3</sub> and NaOH were procured from Merck, Germany. Cr(NO<sub>3</sub>)<sub>3</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, and HCl were purchased from BDH, England. Phosphorus oxychloride (POCl<sub>3</sub>), Triethylamine (HPLC grade; 99%) and Tetrahydrofuran were obtained from Scharlau, Spain and Lobal Chemic laboratory Reagent and Fine Chemicals, India, respectively.

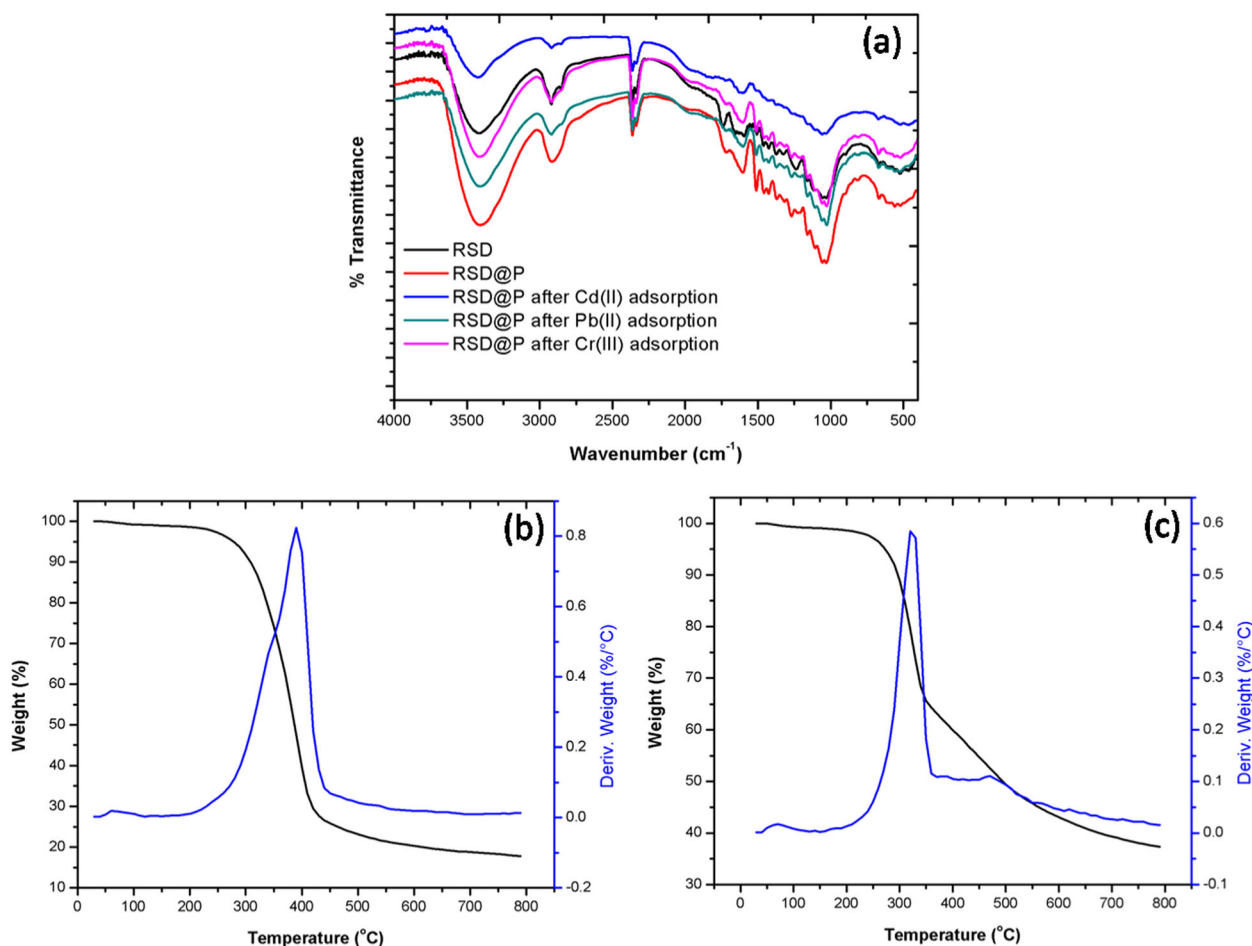
### 2.2 Synthesis of crosslinked phosphorylated raw sawdust

Sawdust was obtained from carpentry workshops and its phosphorylation reaction was carried out by sol–gel method as follows: 3 g of sawdust was added to a mixture containing 10 mL of tetrahydrofuran (THF) and 5 mL of triethylamine (TEA). The mixture was cooled in ice bath with a dropwise addition of 15 mL phosphorus oxychloride to the mixture. The mixture was then refluxed for 1 h. The attained yield was repetitively washed with hot distilled water and dried at 70 °C for 12 h. The obtained product of phosphorylated raw sawdust was designated as (RSD@P).

### 2.3 Adsorption studies

The batch mode experiments were done to test the adsorption of Cd(II), Cr(III), and Pb(II) onto RSD@P. Typically, 15 mg of RSD@P adsorbent was taken in 100 mL conical flask having 25 mL of 25 mg/L from each metal ion separately at 298 K and shaken at 100 rpm for 24 h. After a fixed time interval, an aliquot of the sample was withdrawn from the flask and the concentration of each metal ion in the supernatant was determined by AAS. The % adsorption and  $q_e$  at equilibrium was determined as:

$$\text{Adsorption \%} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$



**Fig. 1** FT-IR spectra of **a** RSD and RSD@P before and after metals adsorption onto RSD@P **b** TGA-DTA curves corresponding to RSD **c** and RSD@P

$$q_e(\text{mg/g}) = (C_o - C_e) \frac{V}{m} \quad (2)$$

The effect of pH on the removal of Cd(II), Cr(III), and Pb(II) metal ions using RSD@P was examined in the pH range of 2 to 10. The effect of contact time on the adsorption of these metals was done in the time range of 1 to 1440 min. Moreover, the effect of initial concentration of the current metal ion adsorption was investigated for diverse  $C_o$  range: 25 to 300 mg/L at different temperatures; 25 to 45 °C.

Desorption experiments were also investigated in batch method. 15 mg of RSD@P was added to 25 mL of 25 mg/L each of metal ions solution under agitation speed of 180 min at 298 K. After 180 min, Cr(III), Cd(II), and Pb(II) metal ions saturated RSD@P sample was isolated from aqueous solution through filtration and it was treated with 25 mL 0.1 M HCl to elute Cd(II), Cr(III), and Pb(II) metal ions. After 180 min, the RSD@P sample was separated from the solution phase and the concentration of metal ions in the solution phase was evaluated using AAS and the percentage

of desorption of these metal ions were found as:

$$\text{Desorption \%} = \frac{\text{Conc. of metal ions desorbed by eluent}}{\text{Initial conc. of metal ions adsorbed on RSD@P}} \times 100 \quad (3)$$

We also tried 0.1 M HNO<sub>3</sub> solutions for the elution of these metal ions using the same procedure mentioned above.

### 3 Results and discussion

#### 3.1 Characterization of RSD and RSD@P

The RSD and RSD@P samples were characterized by SEM-EDX, TEM, FTIR, TGA-DTA, XRD, BET, and XPS and details are given in Text S1 (Supplementary material). Figure 1a shows the FTIR spectra of RSD and RSD@P (before and after adsorption). The strong peak at  $\sim 3423 \text{ cm}^{-1}$  and  $\sim 1662 \text{ cm}^{-1}$  could be accredited to O–H vibrations signifying the

presence of cellulose, hemicellulose and lignin. Peaks at 2918 and 2845 were attributed to C–H stretching vibration of aliphatic compound [21]. The peak at  $1740\text{ cm}^{-1}$  and between  $1589 - 1503\text{ cm}^{-1}$  were allotted to aliphatic carbonyl of xylan hemicellulose, and aromatic rings from lignin, respectively [22, 23]. Also, Fig. 1a showed the finger print region peaks of cellulose, hemicellulose and lignin in the raw sawdust between  $1100$  and  $1800\text{ cm}^{-1}$ . Peaks at  $1370\text{ cm}^{-1}$  and  $1446\text{ cm}^{-1}$  allotted to the C–H stretching vibration of hemicellulose and the C–H bending of the cellulose and lignin, respectively [24]. The peak at  $1232\text{ cm}^{-1}$  was assigned to C–O stretching band indicating the presence of hemicellulose [25]. The peaks at  $1158$  and  $1048\text{ cm}^{-1}$  were assigned to a C–O stretching band of C–O–H group and C–O–C group in the anhydroglucose ring, respectively. After modification of RSD by  $\text{POCl}_3$ , there was a little change in figure. The band in the  $1100$  to  $1200\text{ cm}^{-1}$  region presented in the spectra for P=O group. The peak in the region between  $700$  to  $850\text{ cm}^{-1}$  was probably allotted to the P–O–C bond. The peak at  $2360\text{ cm}^{-1}$  was ascribed to P–H group [26–28].

It can be clearly seen that some changes were noticed in the FT-IR spectra after adsorption of Cd(II), Cr(III) and Pb(II) metal ions onto RSD@P. The decrease and changes in the FT-IR spectra was observed at the peak between  $1100$  to  $1200\text{ cm}^{-1}$  and the bands of  $1176$ – $1040\text{ cm}^{-1}$  after Cd(II), Cr(III), and Pb(II) metal ions adsorption onto RSD@P, the P=O structures at between  $1100$  to  $1200\text{ cm}^{-1}$  was shifted to low. These results suggested that the adsorption between these cations and adsorbent surface was governed by the electrostatic interaction.

**TGA** analysis was accomplished to define the thermal stability of both RDS and RSD@P under inert  $\text{N}_2$  atmosphere. Figure 1b, c shows the TGA with the first derivative of RDS and RSD@P. As can be seen, the thermal degradation of the RDS (Fig. 1b) mainly occurred at temperatures between  $220$  and  $420\text{ }^\circ\text{C}$  and about 73% weight loss was observed. At  $150\text{ }^\circ\text{C}$ , 2% weight loss was noted which assigned to the removal of adsorbed water and residual solvent from the RSD sample [29, 30]. So, the thermal decomposition of RDS was achieved in one step. The observed weight loss was ascribed to the degradation of hemicellulose, cellulose and degradation of lignin [31]. For the RSD@P (Fig. 1c), there are two steps; the first step took place in the temperature range  $250$ – $375\text{ }^\circ\text{C}$ . A weight loss of about 48% was noticed due to the breakdown of hemicellulose and cellulose and degradation of lignin. In the second step, the 10% weight loss observed in the range of temperature between  $400$ – $800\text{ }^\circ\text{C}$  rationally related to the degradation of residual of lignin and phosphoryl group. These two steps indicated the successful modification of RSD by  $\text{POCl}_3$ . The BET surface area and the total pore volume of RSD@P were higher than that of untreated RSD and found to be  $14.56\text{ m}^2/\text{g}$  and  $0.0090\text{ cm}^3/\text{g}$ , respectively.

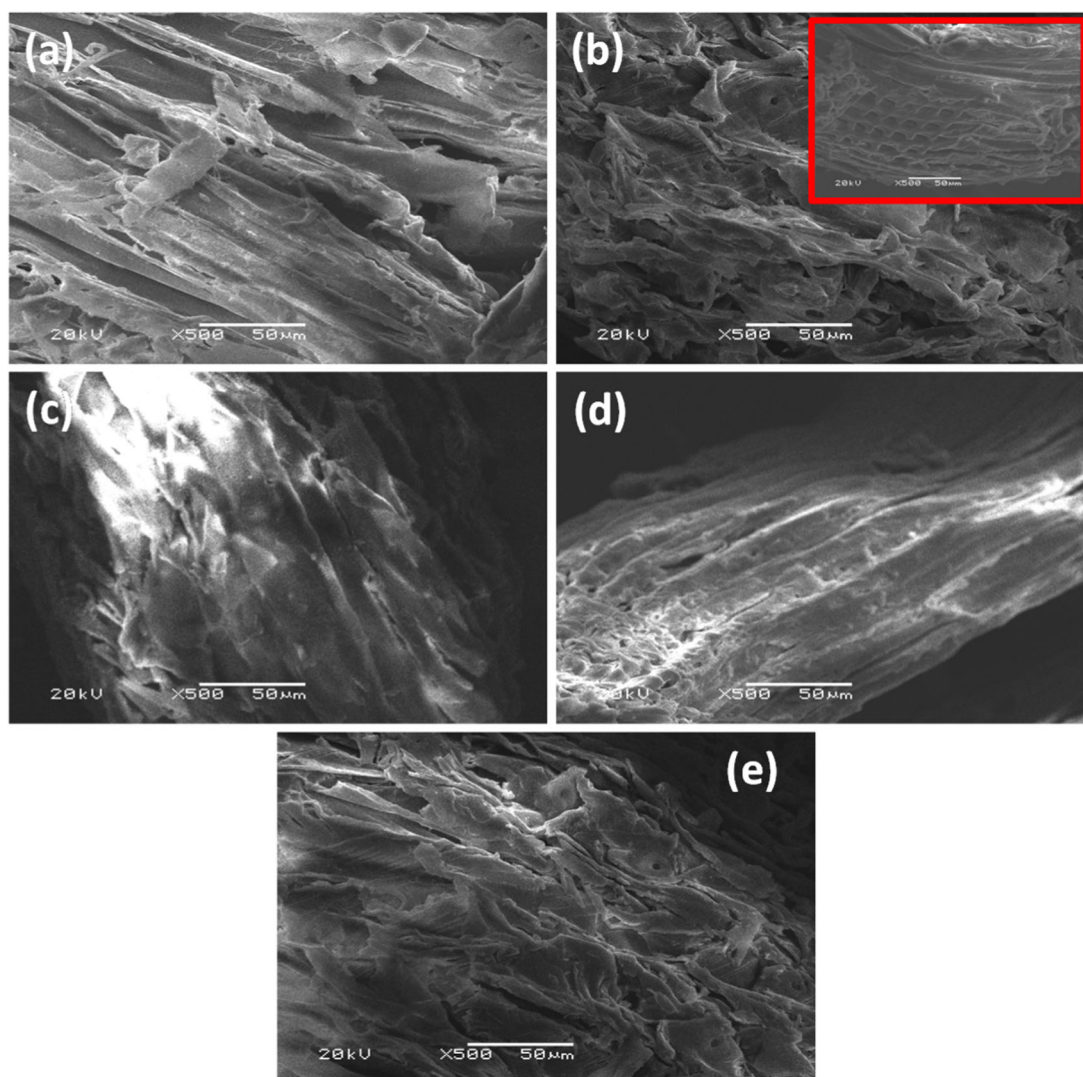
The morphologies of RSD, RSD@P before and after adsorption onto RSD@P are shown in Fig. 2. Smooth morphology and fewer pores were available on the sawdust surface (Fig. 2a). After modification with phosphorus oxychloride ( $\text{POCl}_3$ ), large pores or cavities and channels were observed in the RSD@P (Fig. 2b). After the adsorption of Cd(II), Cr(III), and Pb(II), the surface morphology was changed which might be due to the interaction of these metal ions with the functional groups of RSD@P (Fig. 2c–e). The pores were completely occupied by these metal ions leading to a formation of rough and non-uniform covering over RSD@P surface. These morphological changes confirmed the adsorption of these heavy metal ions onto RSD@P surface.

TEM images of RSD are given in Fig. 3a. The morphology of untreated RSD presented heterogeneous and aggregated surface. The porosity of RSD particles was approximately  $42\text{ nm}$  (Fig. 3a, inset). The particle size of RSD particles was  $22\text{ nm}$  (Fig. 3b). After modification with  $\text{POCl}_3$  (Fig. 3c), a high porosity was observed (Fig. 3c, inset) and the particle size of RSD@P became  $24\text{ nm}$  (Fig. 3d). Also after modified with  $\text{POCl}_3$ , the RSD particles coated by a layer of  $\text{POCl}_3$  (Fig. 3c). The elemental analysis of RSD and RSD@P were performed by EDX analysis (Table 1 and Fig. 4). Untreated RSD spectrum (Fig. 4a) displayed only C and O peaks, while RSD@P spectrum showed the presence of C and O, as well as new peaks of P and Cl (Fig. 4b). This result confirmed the successful modification of RSD by  $\text{POCl}_3$ . The results of elemental composition of RSD@P after adsorption of Cd(II), Cr(III), and Pb(II) showed clearly the presence of Cd(II), Cr(III), and Pb(II) in the structure of the RSD@P.

Figure 5 shows the XPS of RSD and RSD@P. Figure 5a shows two peaks at 284.8 and 530.5 assigning to C 1s and O 1s peaks, respectively for RSD; the RSD@P spectrum shows two additional peaks at 134.3 and 206 eV which might be due to P 2p and C 1s, respectively [32]. The high-resolution spectrum of C 1s, O 1s and P 2p is shown in Fig. 5b. Peaks at 284.6, 285.2, 286.3, 286.5 and 288.1 eV were assigned to C–C, C–OH, C–O, C=O and O=C–O, respectively [33]. On the other hand, peaks at 529.9, 531.3, 532.5, and 534.5 eV corresponded to O=P, O–C, O=C and O=C–O, respectively (Fig. 5c). The peak at 134.3 eV corresponded to P 2p (Fig. 5d) [34]. The presence of P and Cl peaks in RSD@P spectrum also confirmed the successful modification of RSD surface by  $\text{POCl}_3$ .

### 3.2 Adsorption performance

The pH is one of the most essential parameters which effects the surface charge of adsorbent material and metal ion speciation in aqueous solution [35–37]. The effect of solution pH on adsorption process was examined in the pH



**Fig. 2** SEM images of **a** untreated RSD, **b** RSD@P **c–e** RSD@P after adsorption of Cd(II), Cr(III) and Pb(II) metal ions

range of 2–10. Figure 6a displays the effect of pH on the adsorption of Cd(II), Cr(III), and Pb(II) metal ions adsorbed onto RSD@P and rest parameters were kept constants (contact time 1440 min, RSD@P dose 15 mg, temperature 25 °C). The results showed that  $q_e$  for Pb(II) was increased with increasing the pH from 2.0 to 5.8, then it started to decrease. The  $q_e$  was  $3.7 \text{ mg g}^{-1}$  at pH 2 and increased up to  $56.7 \text{ mg g}^{-1}$  at pH 5.8. In the case of Cd(II) and Cr(III), the  $q_e$  was increased until pH 7, then it started to decrease. The  $q_e$  was  $4.6 \text{ mg g}^{-1}$  and  $6.1 \text{ mg g}^{-1}$  at pH 2 which increased up to  $56.2$  and  $57.8 \text{ mg g}^{-1}$  at pH 7 for Cd(II) and Cr(III), respectively. The adsorption of these metal ions was decreased at higher pH which was due to the formation of metal hydroxides [38]. At low pH, the adsorptive removal of these metal ions was low which may be due to the high concentration of  $\text{H}^+$  in the acidic medium, so protonation of the active sites of RSD@P dominated over the adsorption

process. As the pH of the solution increases ( $<7$ ), number of negatively charged sites increased, so that adsorption of these metal ions was increased.

Effect of time on the adsorbed amount of Cd(II), Cr(III), and Pb(II) metal ions using RSD@P adsorbent was studied in the range of 5–240 min as shown in Fig. 6b. It was noted that  $q_e$  of Cd(II), Cr(III), and Pb(II) metal ions was increased with increasing the contact time until the equilibrium was attained (180 min). Adsorption rate was gradually increased up to 180 min for all metal ions. The maximum adsorption capacity for Cd(II), Cr(III), and Pb(II) metal ions was 33.75, 34.40, and 32.7 mg/g, respectively, hence 180 min was enough to reach to equilibrium.

Figure 7 shows the effect of initial concentration of Cd (II), Cr(III), and Pb(II) metal ions (25–300 mg/L) on adsorption at different temperatures (25, 35, and 45 °C). The  $q_e$  of all metal ions was increased with increasing the

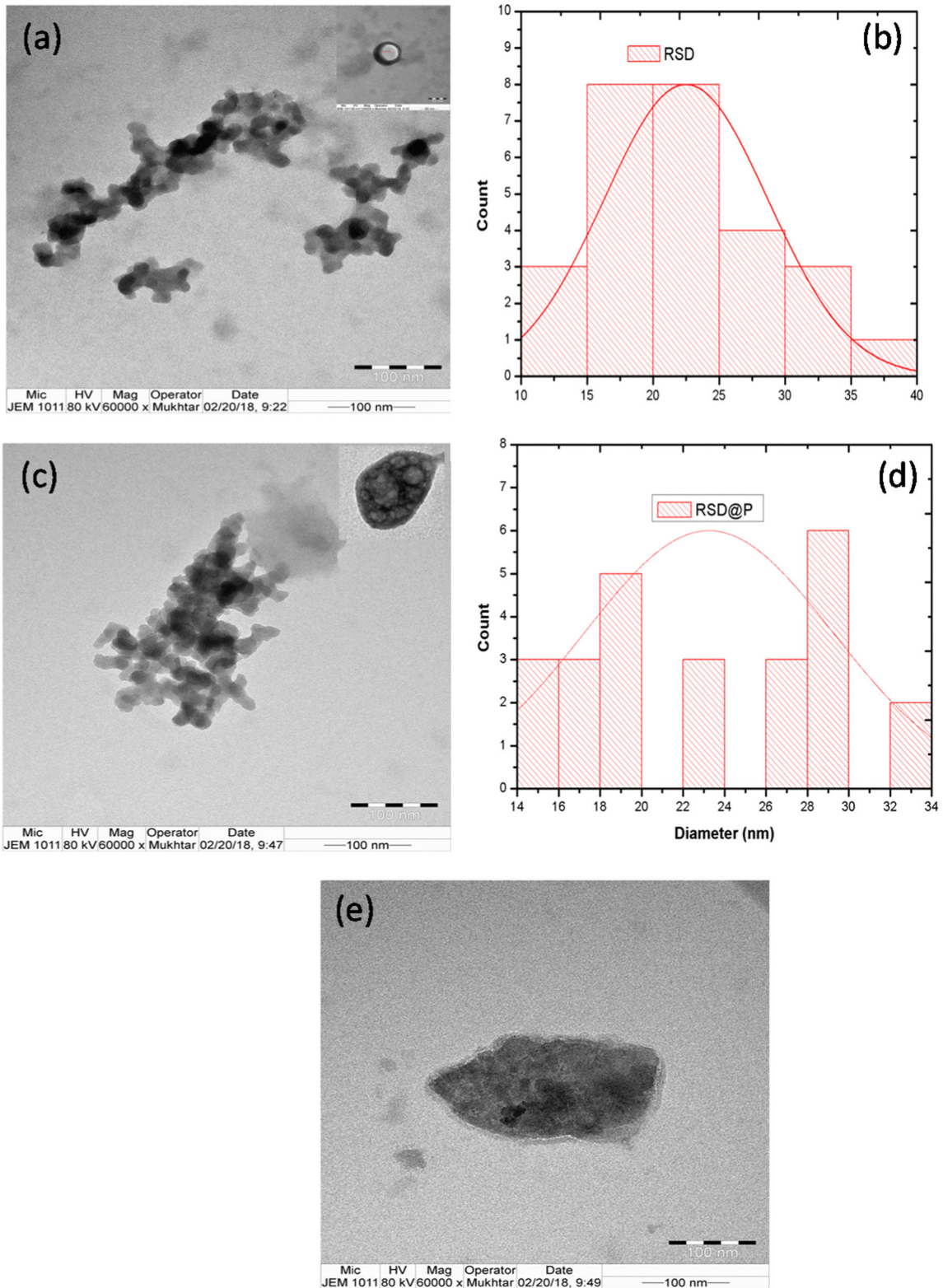
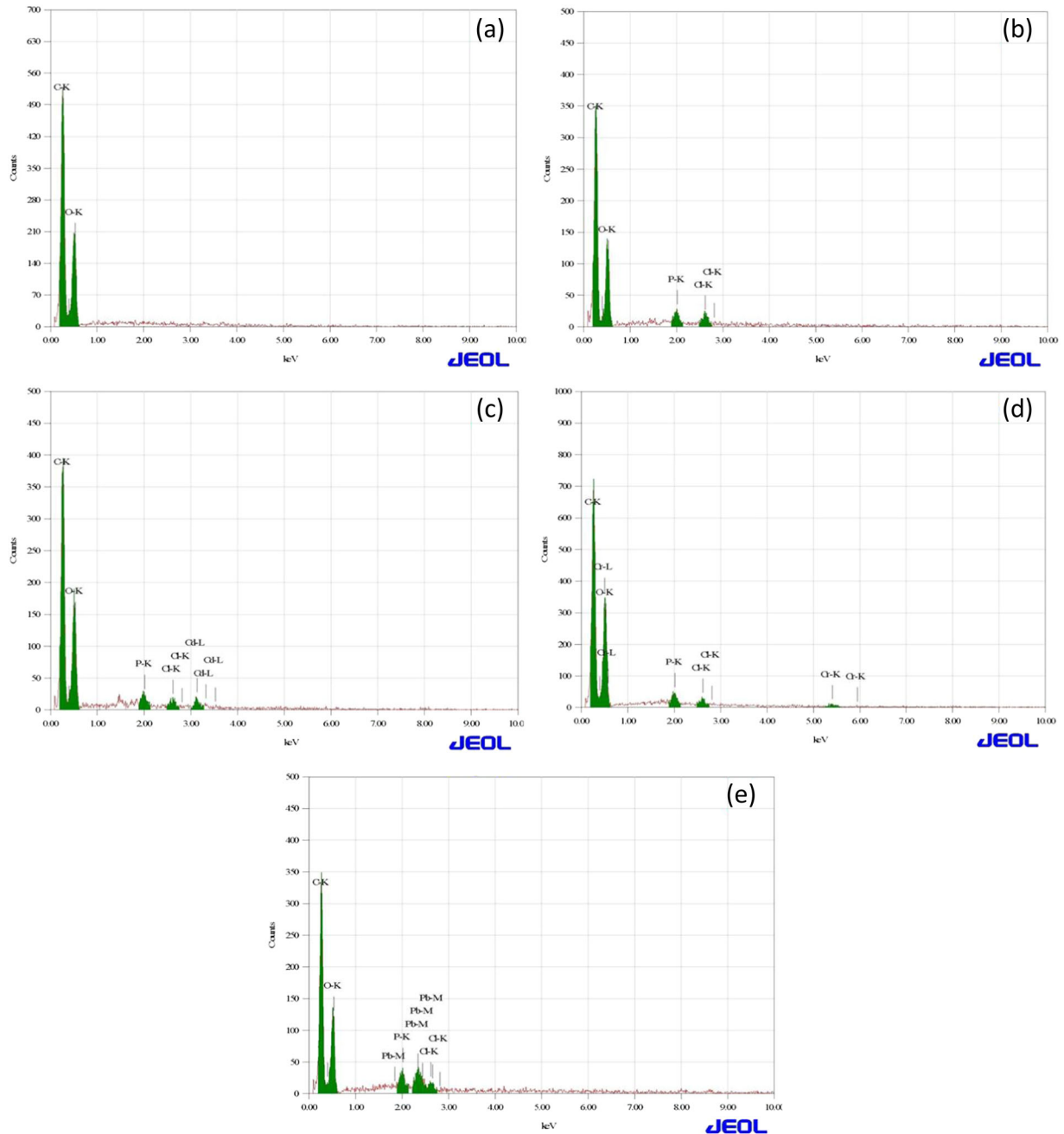


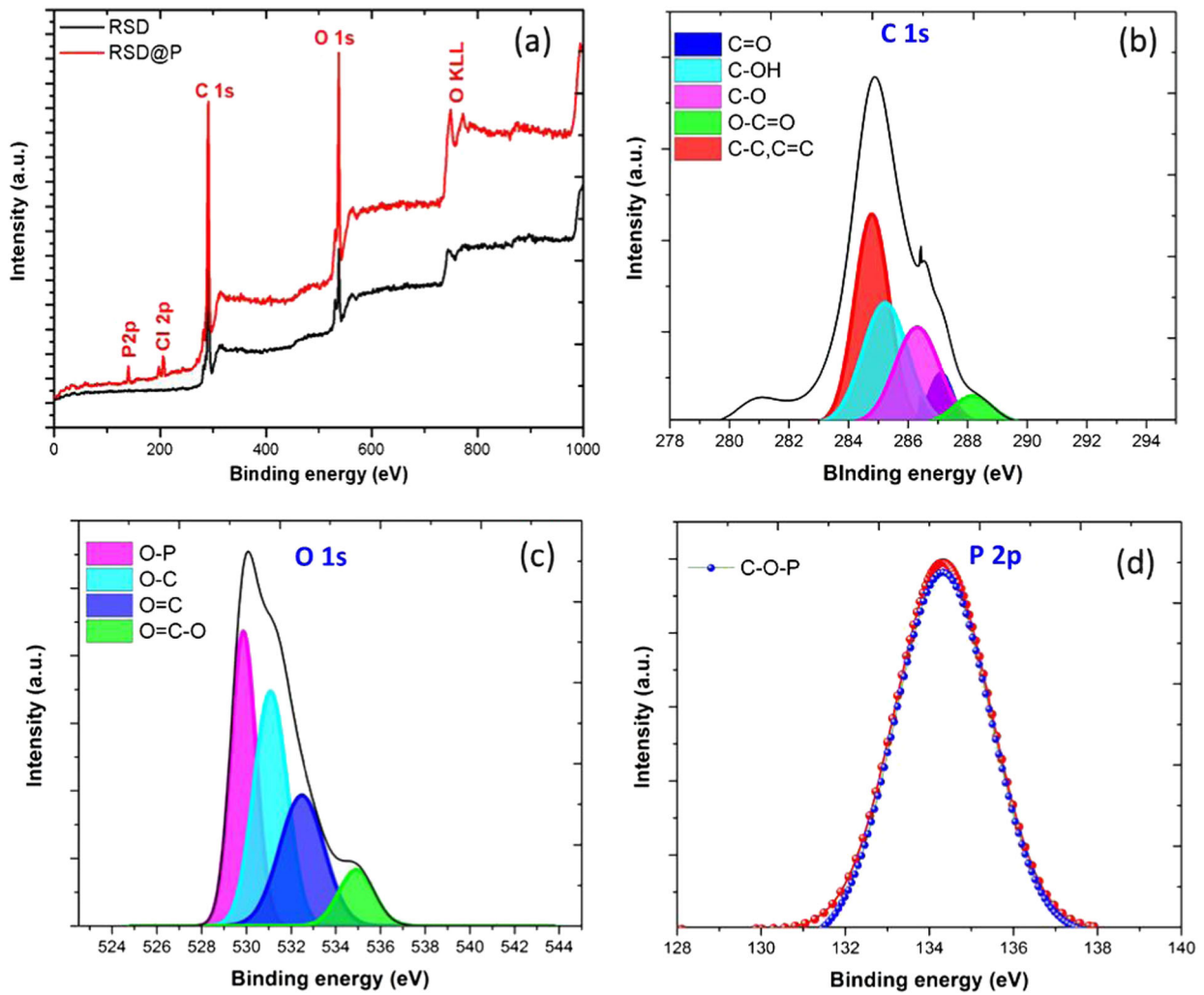
Fig. 3 TEM images and particle size distribution of untreated RSD **a, b** and RSD@P **c–e**, respectively

**Table 1** Elemental analysis of RSD, RSD@P, and saturated RSD@P after the adsorption of heavy metals

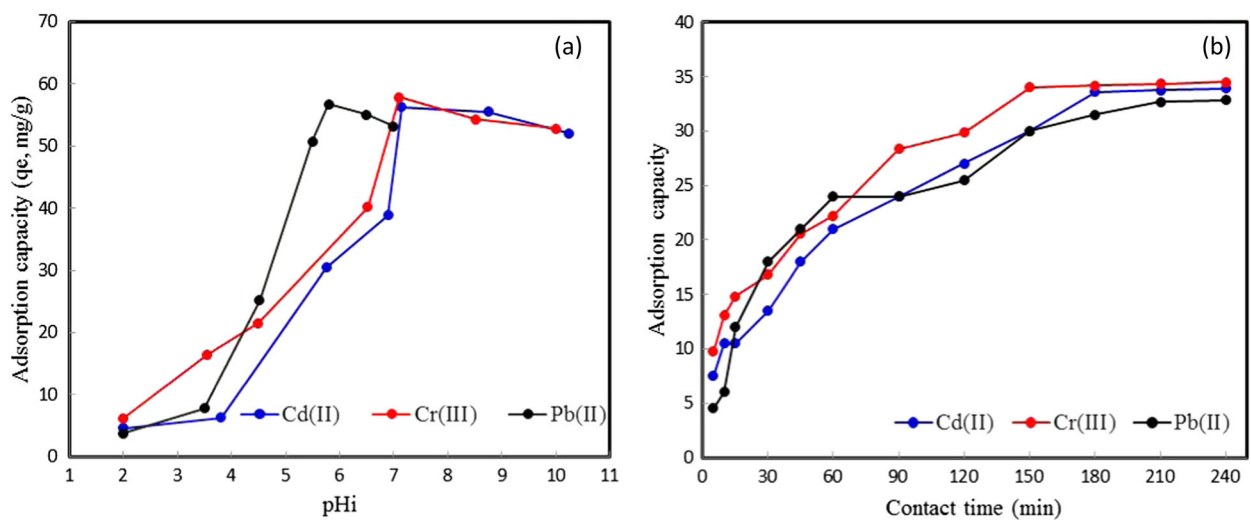
| Sample          | Elemental content (%) |       |      |      |      |      |      |
|-----------------|-----------------------|-------|------|------|------|------|------|
|                 | C                     | O     | P    | Cl   | Cd   | Cr   | Pb   |
| RSD             | 51.30                 | 48.70 | –    | –    | –    | –    | –    |
| RSD@P           | 48.57                 | 50.24 | 0.65 | 0.54 | –    | –    | –    |
| RSD@P + Cd(II)  | 52.23                 | 45.54 | 0.46 | 0.37 | 1.41 | –    | –    |
| RSD@P + Pb(II)  | 51.53                 | 44.60 | 0.73 | 0.50 | –    | –    | 2.64 |
| RSD@P + Cr(III) | 53.93                 | 44.63 | 0.65 | 0.47 | –    | 0.32 | –    |

initial metal ion concentration, while the percent adsorption of these metal ions displayed the opposite trend. Once, the initial concentration of Cd(II), Cr(III), and Pb(II) metal ions was increased from 25 to 300 mg/L, the  $q_e$  was increased from 28.75 to 162.50 mg g<sup>-1</sup>, 29.37 to 213.07 mg g<sup>-1</sup>, and 28.37 to 148.88.50 mg g<sup>-1</sup> at 25 °C, respectively. The increase in the adsorption capacity with increasing initial metal concentrations could be attributed due to the accessibility of vacant sites for metal binding [39–41]. It can be concluded that RSD@P is able to bind Cd(II), Cr(III), and

**Fig. 4** EDX images of **a** untreated RSD, **b** RSD@P **c–e** RSD@P after adsorption of Cd(II), Cr(III), and Pb(II) metal ions



**Fig. 5** a X-ray photoelectron spectroscopic images of RSD and RSD@P; High-resolution XPS spectrum for **b** C 1s, **c** O 1s, **d** P 2p



**Fig. 6** Removal of Cd(II), Cr(III), and Pb(II) metal ions using RSD@P at different **a** pH and **b** time



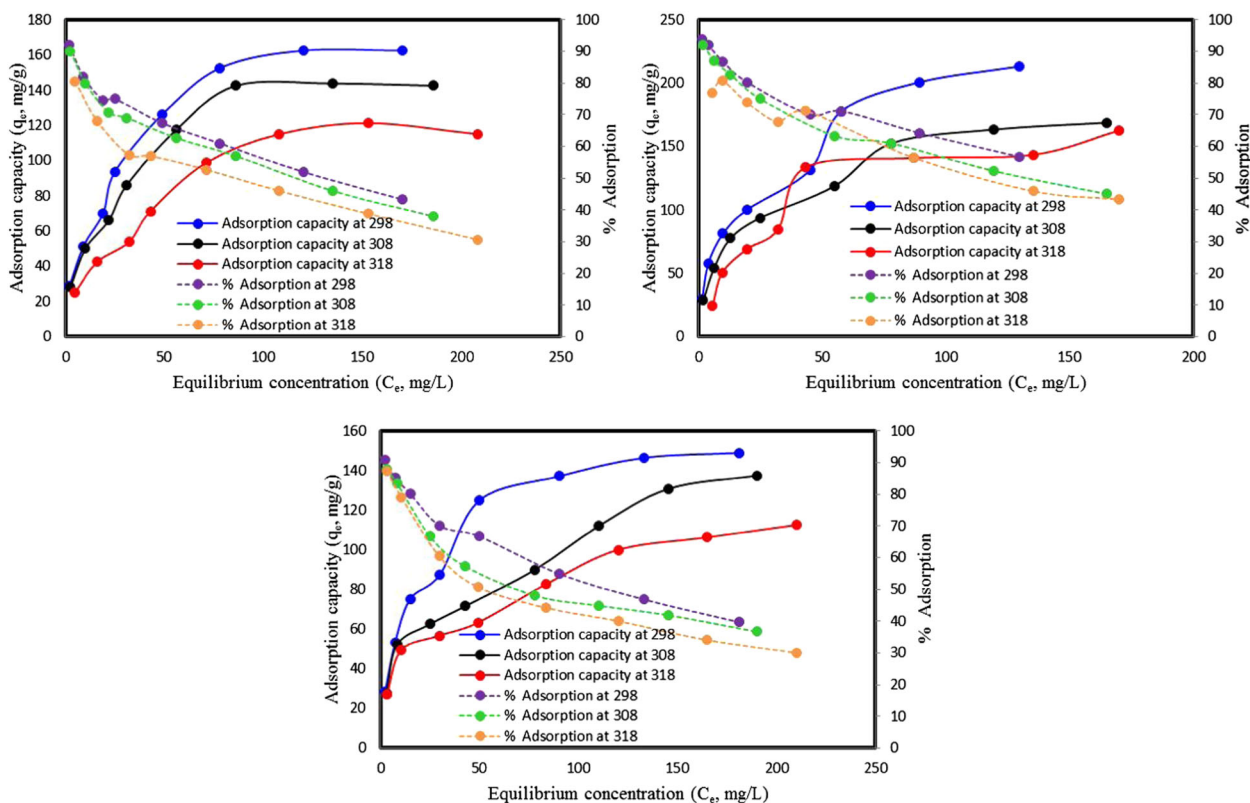


Fig. 7 Effect of concentration on the adsorption capacity of Cd(II), Cr(III), and Pb(II) using RSD@P at different temperatures

Table 2 Isotherm parameters for the adsorption of Cd(II), Cr(III), and Pb(II) metal ions onto RSD@P

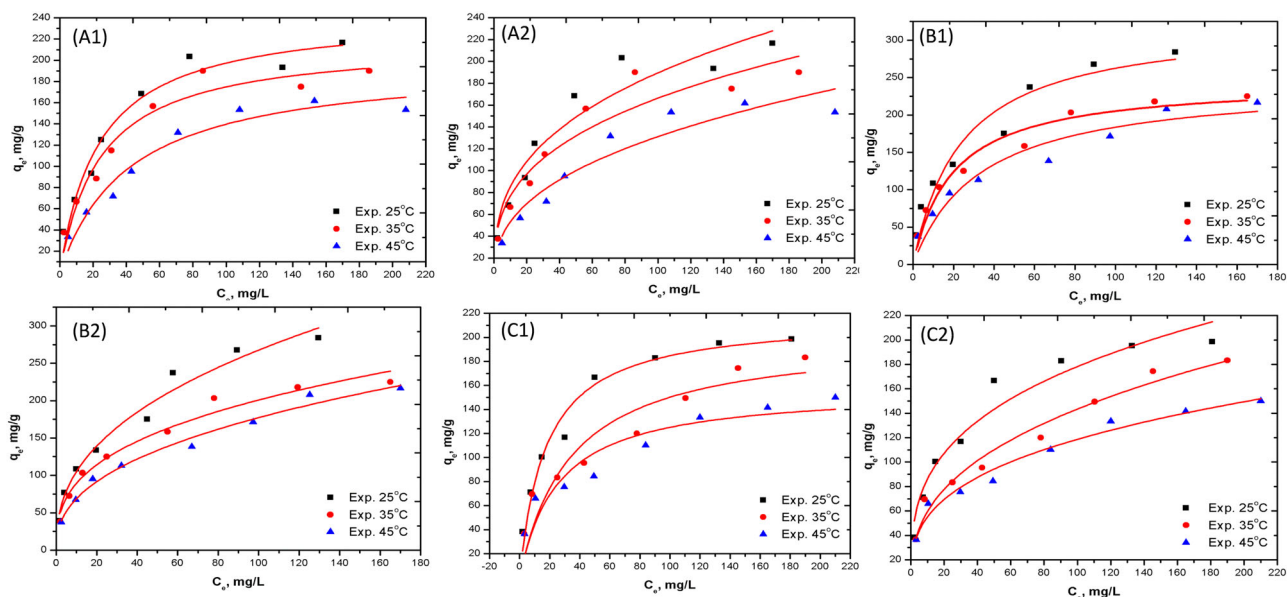
| Metal ions | Temperature (K) | $q_m$ , exp. (mg/g) | Langmuir isotherm  |       |       | Freundlich isotherm               |      |       |
|------------|-----------------|---------------------|--------------------|-------|-------|-----------------------------------|------|-------|
|            |                 |                     | $q_m$ , cal (mg/g) | $K_L$ | $R^2$ | $K_f$ (mg/g)(L/mg) <sup>1/n</sup> | $N$  | $R^2$ |
| Cr(III)    | 298             | 284.1               | 325.0              | 0.042 | 0.933 | 41.23                             | 2.46 | 0.973 |
|            | 308             | 225.0               | 245.4              | 0.051 | 0.958 | 39.82                             | 2.84 | 0.972 |
|            | 318             | 216.66              | 244.8              | 0.030 | 0.928 | 26.88                             | 2.44 | 0.983 |
| Cd(II)     | 298             | 284.1               | 244.3              | 0.042 | 0.959 | 38.32                             | 2.89 | 0.923 |
|            | 308             | 190.0               | 217.9              | 0.041 | 0.945 | 35.48                             | 2.98 | 0.896 |
|            | 318             | 153.33              | 198.8              | 0.024 | 0.950 | 21.54                             | 2.55 | 0.912 |
| Pb(II)     | 298             | 198.51              | 217.0              | 0.057 | 0.965 | 41.74                             | 3.17 | 0.986 |
|            | 308             | 183.33              | 201.2              | 0.024 | 0.857 | 24.79                             | 2.62 | 0.971 |
|            | 318             | 150.0               | 157.2              | 0.038 | 0.852 | 25.66                             | 3.01 | 0.973 |

Pb(II) metal ions over a wide range of concentrations. Moreover, the  $q_e$  was decreased with increasing the temperature from 25 to 45 °C, confirmed the exothermic nature of adsorption process [33].

### 3.3 Adsorption isotherms

The behavior of Cd(II), Cr(III), and Pb(II) metal ion adsorption, as well as their interaction onto RSD@P was performed using Freundlich [42] and Langmuir models [43] and the information concerning the models is given in

Supplementary Information (Text S2). The isotherm data concerning the adsorption of these metal ions on RSD@P is presented in Table 2. On the basis of the correlation coefficient ( $R^2$ ) values, Freundlich isotherm showed a better fit of experimental data than that of Langmuir isotherm models at all temperatures (except Cd(II)) which showed the existence of multilayer surface condition (Fig. 8) [44]. It can be observed that values of  $K_f$  of Freundlich isotherm constants were decreased with increasing temperature from 298 to 318 K, implying that the adsorption was exothermic in nature. The maximum calculated monolayer adsorption



**Fig. 8** Non-linear isotherm models for Cd(II), Langmuir (A1), Freundlich (A2); Cr(III), Langmuir (B1), Freundlich (B2) and Pb(II), Langmuir (C1), Freundlich (C2)

**Table 3** Comparison of adsorption capacity of RSD@P with other sawdust adsorbents

| Adsorbent       | Maximum monolayer adsorption capacity (mg/g) |         |        | References |
|-----------------|--|---------|--------|------------|
|                 | Cd(II)                                       | Cr(III) | Pb(II) |            |
| Meranti sawdust | –  | 37.878  | 34.246 | [5]        |
| Sawdust         | 73.6   | –       | –      | [45]       |
| Sawdust         | 41.21  | –       | –      | [46]       |
| sawdust         | –  | –       | 30.48  | [47]       |
| Sawdust biochar | –  | 43.48   | –      | [48]       |
| sawdust         | 5.76   | –       | 15.90  | [49]       |
| RSD@P           | 244.3  | 325.0   | 217.0  | This work  |

capacity ( $q_m$ ) of Cd(II), Cr(III), and Pb(II) metal ions on RSD@P using Langmuir equation were 163.9, 222.2, and 166.6 mg/g at 298 K, respectively. Comparing these data for RSD@P with that obtained for adsorption of the same metal ions by several raw sawdust is shown in Table 3 [5, 45–49]. It was observed that the values of  $q_m$  using RSD@P was better than that of other adsorbents used for same metal ions.

### 3.4 Adsorption kinetics and thermodynamics parameters

Adsorption kinetics were performed using pseudo-first-order [50] and the pseudo-second-order models [51] (Supplementary Information (Text S3)). Table 4 shows the kinetic data for the adsorption of these metal ions on

RSD@P. It can be seen that values of the correlation coefficient ( $R^2$ ) was well fitted to pseudo-second-order. Similar results were reported for the adsorption of Cd(II), Co(II), and Pb(II) [16]. The plots for these two models are given in Fig. 9.

The details of the thermodynamic parameters are given in Supplementary Information (Text S4). Table 5 shows the thermodynamic parameters such as ( $\Delta H^\circ$ ), ( $\Delta S^\circ$ ), and ( $\Delta G^\circ$ ) for the adsorption of Cd(II), Cr(III), and Pb(II) metal ions using RSD@P that were estimated at  $C_o$  (50, 100, and 150 mg/L). The negative values of  $\Delta G^\circ$  insured the spontaneous adsorption of Cd(II), Cr(III), and Pb(II) metal ions onto RSD@P. The increase of  $\Delta G^\circ$  with increasing temperature explained a more efficient adsorption process at lower temperature. The negative value of ( $\Delta H^\circ$ ) and ( $\Delta S^\circ$ ) designated the exothermic adsorption and decrease in the randomness between the interfaces.

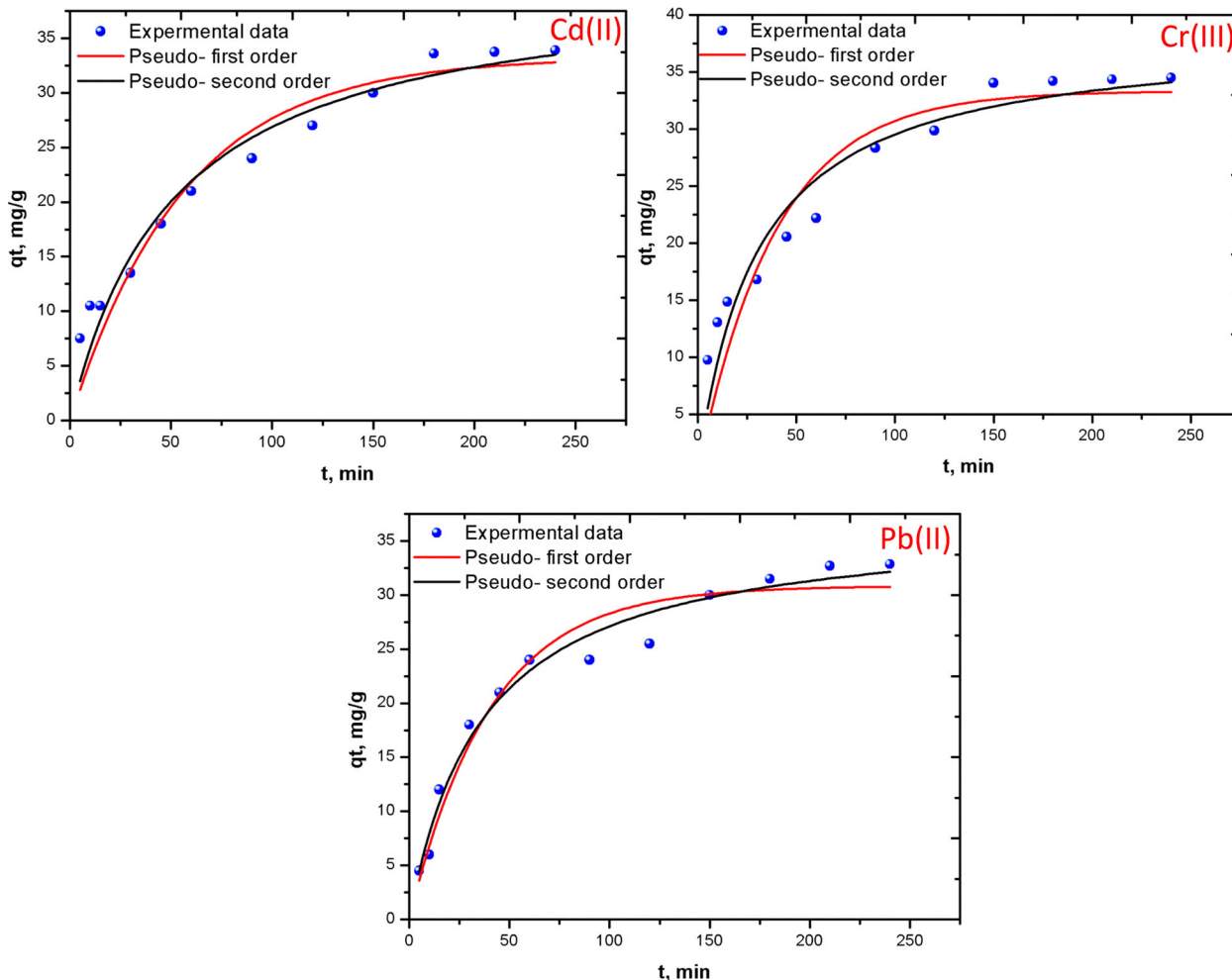
### 3.5 Adsorption mechanism and desorption studies

Figure 10 shows the mechanism of adsorption–desorption behavior for removal of Cd(II), Cr(III), and Pb(II) metal ions onto RSD@P from aqueous medium. The type of interaction was electrostatic attraction between electron-rich oxygen onto surface of RSD@P and electropositive metal.

Adsorption–desorption experiments were conducted to evaluate the possibility of regeneration and reuse of the RSD@P using 0.1 M HCl/HNO<sub>3</sub>. As shown in Fig. S1, 0.1 M HCl solution exhibited the better elution and recovery. The maximum desorption of Cd(II), Cr(III), and Pb(II) by using 0.1 M HCl were 86.96, 90.44, and 88.69%,

**Table 4** Kinetic model constants for the adsorption of Cd(II), Cr(III), and Pb(II) metal ions onto RSD@P

| Metal ions | $C_0$ , mg/L | $q_e$ , exp | Pseudo-first-order |                            |       | Pseudo-second-order               |   |       |
|------------|--------------|-------------|--------------------|----------------------------|-------|-----------------------------------|---|-------|
|            |              |             | $q_e$ , cal        | $K_1$ (min <sup>-1</sup> ) | $R^2$ | $q_e$ , cal (mg g <sup>-1</sup> ) | $K_2$ (g mg <sup>-1</sup> min <sup>-1</sup> ) | $R^2$ |
| Cr(III)    | 25           | 34.05       | 33.33              | 0.0254                     | 0.865 | 38.33                             | 0.00087                                       | 0.934 |
| Cd(II)     | 25           | 33.6        | 33.26              | 0.0178                     | 0.924 | 40.64                             | 0.00048                                       | 0.952 |
| Pb(II)     | 25           | 35          | 30.80              | 0.0203                     | 0.953 | 37.02                             | 0.00073                                       | 0.979 |



**Fig. 9** Non-linear kinetic models for the adsorption of Cd(II), Cr(III), and Pb(II) metal ions onto RSD@P

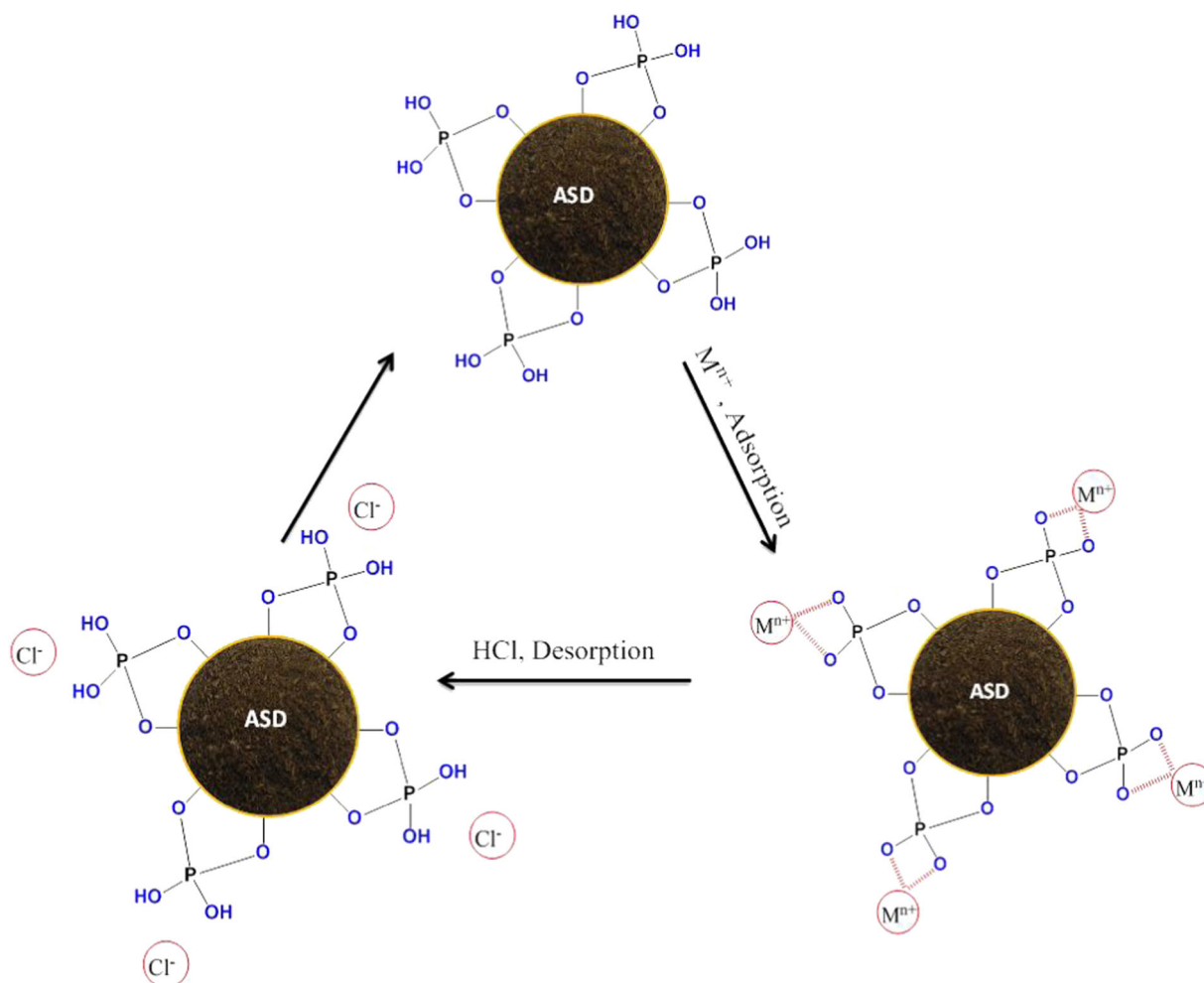
**Table 5** Thermodynamic parameters for the adsorption of Cd(II), Cr(III), and Pb(II) metal ions onto RSD@P

| Metal ions | $C_0$ , mg L <sup>-1</sup> | $-\Delta H^\circ$ (KJ/mol) | $-\Delta S^\circ$ (J/mol.K) | $-\Delta G^\circ$ (KJ/mol) |       |       |
|------------|----------------------------|----------------------------|-----------------------------|----------------------------|-------|-------|
|            |                            |                            |                             | 298 K                      | 308 K | 318 K |
| Cr(III)    | 50                         | 40.03                      | 114.03                      | 6.06                       | 4.88  | 3.79  |
|            | 100                        | 25.86                      | 7.5027                      | 3.47                       | 2.81  | 1.97  |
|            | 150                        | 24.92                      | 76.508                      | 2.09                       | 1.39  | 0.57  |
| Cd(II)     | 50                         | 29.81                      | 86.74                       | 3.75                       | 3.54  | 1.99  |
|            | 100                        | 32.07                      | 98.15                       | 2.72                       | 2.04  | 0.74  |
|            | 150                        | 24.19                      | 74.86                       | 1.79                       | 1.32  | 0.282 |
| Pb(II)     | 50                         | 16.705                     | 41.24                       | 4.35                       | 4.132 | 3.51  |
|            | 100                        | 32.07                      | 98.15                       | 2.09                       | 0.046 | 0.069 |
|            | 150                        | 24.191                     | 7.48                        | 1.72                       | 0.34  | 0.624 |

respectively, while it was 69.50, 73.91, and 71.24%, respectively in the case of 0.1 M HNO<sub>3</sub>. This result could be ascribed to the size of ions because Cl<sup>-</sup> is smaller in comparison to NO<sub>3</sub><sup>-</sup> ions [52].

### 4 Conclusions

In the present work, the crosslinked phosphorylated raw sawdust was successfully synthesized and used for the removal of Cd(II), Cr(III), and Pb(II) from aqueous medium. The results showed that RSD@P was an effective,



**Fig. 10** Mechanism for the adsorption–desorption for Cd(II), Cr(III), and Pb(II) metal ions using RSD@P

economical and efficient adsorbent for capturing Cd(II), Cr(III), and Pb(II) metal ions from aqueous solution. The maximum Langmuir adsorption capacity for Cd(II), Cr(III), and Pb(II) metals onto RSD@P was 244.3, 325, and 217 mg/g, respectively at 298 K. The adsorption isotherm and kinetics data revealed that Cd(II), Cr(III), and Pb(II) metal ions were well fitted to Freundlich isotherm and pseudo-second-order kinetic models. The adsorption of Cd(II), Cr(III), and Pb(II) was physicochemical process involving important electrostatic attractions. The desorption results exhibited the best recovery of these metal ions using 0.1 M HCl.

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### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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