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Elaboration of balance through adsorption of cadmium and selenium between water and underlying sediments via their analysis in drinking, wastewater and sediment samples

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ABSTRACT

There is a very delicate balance between water and the underlying sediments as far as adsorption/desorption is concerned. The toxicity of heavy elements (HEs) in water is significant because of their non-biodegradability. The nature mostly takes care of this as HEs tend to remain adsorbed in the underlying sediments as compared with the water column above them. In the present work, cadmium (Cd) and selenium (Se) have been monitored in the drinking water and sediment samples taken from Rawal dam (Islamabad, Pakistan), wastewater and sediment samples taken from Nullah Lai (Rawalpindi, Islamabad). Results show that the respective mean values for the metals under consideration are far more in the underlying sediments than in the water column above them; the mean value of Cd in drinking water samples taken from Rawal dam is 0.74 $\mu g \cdot L^{-1}$ and that of Se is 1.37 $\mu g \cdot L^{-1}$. Mean value of Cd and Se concentration in wastewater samples taken from Nullah Lai are 3.6 and 4.8 $\mu g \cdot L^{-1}$ while range of these elements are 2.8–4.2 and 4.2–5.8 $\mu g \cdot L^{-1}$, respectively. Mean value of Cd and Se concentration in sediment samples taken from Rawal dam are 1.12 and 0.35 $\mu g \cdot g^{-1}$, respectively. Mean value of Cd and Se concentration in sediment samples taken from Nullah Lai are 4.95 and 0.7 $\mu g \cdot g^{-1}$, respectively. To elaborate the balance between water and sediments, the immobilization of Cd and Se has been studied on Sawaan River's sand. The rate constant for the sorption of Cd(II) and Se(IV) onto the Sawaan River sand is $(2.13 \pm 0.8) \times 10^{-1}$ min^{-1} and $(3.75 \pm 0.12) \times 10^{-2}$ min^{-1}, respectively. The sorption energy E for the sorption of Cd(II) is 11.80 ± 0.25 kJ·mol^{-1} while the sorption of Se(IV) is 8.93 ± 0.04 kJ·mol^{-1}. The results of analysis, kinetic and thermodynamic data from adsorption procedure show that sands can effectively be used as preconcentrating agents as well as adsorbents for removal of toxic elements from water and also nature has its own system of minimizing pollutants from the environment.

Keywords: Analysis; Cadmium; Differential pulse voltammetry; Atomic absorption spectrophotometry; Sediments; Selenium; Adsorption; Kinetics; Thermodynamics

1. Introduction

Compared with the water column, the underlying aquatic sediments sorb the toxic chemicals especially the heavy metals to a greater extent [1]. Heavy metals once entered into environment, can exist in various chemical forms under different conditions and are not completely removed or converted to non-toxic derivatives [1,2]. Most of the metals have toxic effect only when their concentrations reach above the threshold values recommended by the WHO but a few metals are toxic merely due to their presence [3]. Cadmium belongs to the

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latter category while selenium has a delicate borderline position being essential but also toxic at the same time. Excessive amount of cadmium (Cd) and selenium (Se) can have adverse effects on the health of living beings [4,5]. Sediments form a sink for soluble trace metals and therefore may reflect the trace metal content of the over lying water [6,7]. In the present study, drinking, wastewater and sediment samples from Rawal dam and Nullah Lai are taken to confirm the distribution of Cd and Se in them. Rawal dam is a freshwater artificial reservoir providing drinking water to the twin cities of Pakistan, named Islamabad the capital and Rawalpindi which is adjacent to the capital. An ArcGIS map shown in Fig. A1 can be informative regarding the location of this dam. Nullah Lai is a natural rainwater fed stream which extends into the twin cities, considered a waste carrier having catchment area of about 234.8 km^2. Fig. A1 shows the location of Nullah Lai. For the analysis of selenium in water and sediments, only differential pulse cathodic stripping voltammetry (DPCSV) has been employed, but for cadmium, differential pulse anodic stripping voltammetry (DPASV) has been utilized for determination of Cd in drinking water while atomic absorption spectrometry (AAS) for determination in wastewater as well as sediment samples. A general assessment of water regarding hardness, alkalinity, pH, total dissolved solids, calcium and sodium content has also been carried out as the physical parameters influence the amount of heavy metals adsorbed or desorbed [8]. The immobilization pattern for both the elements has been studied onto the Sawaan River sand (SRs) which enables to find out the kinetics and thermodynamics involved in keeping this balance [9–11]. Fig. A1 has the location information of Rawal dam, Nullah Lai and SRs. The present work is planned to highlight the significance of sediments which act as a natural sink for heavy and toxic elements especially for under developed countries as there is hardly any system of domestic and industrial effluent treatment before it enters the main water streams. The major hypothesis of this work is that the safer water column above the sediments is ensured by the underlying sediments. If the sediments are not capable of sorbing the toxic substances, the overlying water will face greater pollution. However, since a slight change in the physical parameters such as temperature and pH can disturb the sorption pattern, therefore, the optimization of all these aspects has been executed in this work.

2. Experimental

2.1. Reagents and chemicals

High purity grade (in almost all cases purity ≥99%) commercially procured chemicals mainly from Merck (Germany) were utilized for the present study. The stock solutions were prepared using oxides of cadmium and selenium which were digested in suitable media. Hydrochloric, nitric, perchloric acids and hydrogen peroxide, were used for digestion of water and sediment samples. Standard reference materials (SRMs) used were IAEA soil sample-1 and NBS-1645 sediment sample while SRs was employed for the immobilization.

2.2. Equipment

A model 174A polarographic analyzer from Princeton Applied Research, USA, equipped with hanging mercury drop electrode model-6.355.000 from Metrohm, Switzerland, and XY-recorder RE0089 from Princeton Applied Research, USA, was used for the DPASV and DPCSV. A Varian (Model SpectrAA 300/400, Australia) atomic absorption spectrometer was employed for AAS. Some of the other instruments used in the study were pH meter (Metrohm 605, Switzerland), conductivity meter (Wescan model 212, USA), flame photometer (Jenway PFP-7, UK; for the Na estimation), digital analytical balance from Mettler, Switzerland, with a detection limit of 0.1 mg.

2.3. Standard reference materials

Table A1 shows the results of SRMs analysis for Cd and Se using the abovementioned techniques. It is clearly indicated that the techniques and the methodology that has been used in this project gives accurate results.

2.4. Sample collection and preservation

Water and sediment samples were collected from various locations of the Rawal dam (a freshwater reservoir for the twin cities) and also from Nullah Lai (wastewater stream that carries domestic, industrial and farm effluents of the twin cities). For further elaboration, the sample collection points with description have been given in Tables A2 and A3. Samples were collected in different bottles for the analysis of metals and for other constituents. For the collection of water samples for metal analysis, 1–2 mL of $HClO_4$ was added into the bottles to avoid any losses. For the collection of water samples for other constituents either the samples were analyzed immediately after collection or stored in deep freezer at about –20°C and thawed again before analysis.

2.5. Pretreatment of sediment and Wastewater samples

Many combinations of different acids were tried for effective digestion of the sediment samples and thereby recovery of the sought for elements [12–14]. However, the recovery of sought for element was better and sharper peaks were observed in the voltammograms for one combination (i.e., $HNO_3 + HClO_4 + H_2O_2$). Table A4 shows the effect of the acid combinations. The recovery of elements is checked by spiking 10 and 20 ($\mu g\ L^{-1}$) of the same element's solution prepared in the laboratory (Table A5).

2.6. Immobilization of Cd and Se on Sawaan River sand

The conditions for Cd and Se immobilization were optimized using the basic principles of adsorption. For the batch adsorption study, a water-bath temperature controlled shaker was used. For each case a known volume of the Cd(II) and Se(IV) ion stock solutions was diluted with 10 mL of doubly deionized water. Further this solution was agitated with 100 mg adsorbent which was already optimized on a Stuart mechanical shaker at 700 rpm for an optimum time to effect equilibration. The resulting mixture was then centrifuged at 5,000 rpm to obtain phase separation. A portion of the supernatant solution was withdrawn and the Cd(II), Se(IV) ion concentration measured by differential pulse voltammetry to establish the equilibrium concentration (C_e) and also the initial concentration (C_0). The distribution coefficient values can be calculated from:

$$\mathrm{Rd} = \frac{\text{Amount of metal on adsorbent}}{\text{Amount of metal in solution}} \times \frac{\text{Volume of Solution (V)}}{\text{Weight of dry adsorbent (w)}}\,\mathrm{cm}^3/\mathrm{g} \qquad (1)$$

2.7. Pretreatment of sand

The SRs (employed as a natural adsorbent in the present study) was collected from Chirah located in the Islamabad/Rawalpindi region. The sand was processed by washing it with the deionized water and drying in an oven at about 100°C for about 8 h. The processed sand was then passed through a 100 mesh sieve to have it of comparable size to that of the carbon (graphite) employed in this study. The average Brunauer-Emmett-Teller surface area was found to be 1.54 m^2g^{-1}; other descriptions of the sand are; its fine grained nature with about 40% feldspar, 30% quartz, 15% rock fragments and 5% (mica + hematite) while magnetite and other heavy minerals constitute rest of the 10%.

3. Results and discussion

The results of present study will be discussed in the following sections. Starting from the analysis part, the study will carry on elaborating the distribution of ions between water and sediments through adsorption.

3.1. Drinking water and sediment samples

Drinking water (Rawal dam) and sediments' samples were drawn out from different areas of Rawal dam. In Table 1, selenium is not recorded in four areas and cadmium in two areas referring to the fact that in these areas the concentrations are below the detection limit of the instrument, and therefore negligible. Observing the pattern of the determined concentrations, $(Rw)_1$ and $(Rw)_2$ which have higher concentrations of Cd and Se, these are the places in which the water is in direct and close contact with the sediments while $(Rw)_6$ is again a point where water goes through the inlet pool for filtration. All values of pH, conductance and total dissolved solids are within the same range, a quality which is important for drinking water sources. pH for all the samples is very close to neutral zone. A study carried out on adsorption confirms that this kind of pH favours adsorption and due to adsorption in the natural system the heavy elements (HEs) do not enter the water environment rather they prefer remaining in the sediments [15]. Those samples which were in close contact with the sediments have also been studied for these elements in their sediments. Table 1 also gives us the comparison of concentrations in water as well as sediments. This comparison clearly indicates that the sediments have a greater ratio of elements as compared with the water, which in return show that at such conditions of pH, temperature, conductance and TDS, the HEs tend to remain in the sediments.

3.2. Wastewater and sediment samples

Nullah Lai carries the waste material of Rawalpindi and Islamabad region in Pakistan. Important is the fact that not only domestic garbage but also some industrial and workshop effluents enter into this stream. Since the values for various regions were not very different, therefore, only few samples have been reported for this analysis. It can be observed that in the wastewater samples there is a greater concentration of these elements. Table 2 carries the information regarding concentrations of Cd and Se in Nullah Lai, it also depicts the general analysis of wastewater samples. pH, conductance and TDS values indicate that effluents have largely been released to this wastewater stream. Greater values of conductivity and TDS show that many dissolved conducting substances are poured from the household, industrial and workshop effluent outlets. If we compare with Table 1, the sediment samples have greater concentrations of the elements as compared with the water samples from same water stream. It is clear that such pH values and presence of different types of ions support lesser adsorption of HEs into the sediments. Rather the HEs would tend to be in desorbed form, which of course is a reason of water pollution.

3.3. Statistical parameters of analysis

Various parameters are jotted down in Table 3 for samples collected from the Rawal dam. These values show that this water is safe for drinking as it is given out to various areas of Islamabad and Rawalpindi. But if the problem is detected in any area, it may be due to the mixing up of waste and drinking water pipes, or corrosion of pipes or

Table 1
Concentration and general analysis in the water samples of Rawal dam

$(Rw)_{No}$	Cd in water ($\mu g{\cdot}L^{-1}$)	Cd in sediments ($\mu g{\cdot}g^{-1}$)	Se in water ($\mu g{\cdot}L^{-1}$)	Se in sediments ($\mu g{\cdot}g^{-1}$)	pH	Conductivity ($\mu S{\cdot}cm^{-1}$)	TDS ($\mu g{\cdot}mL^{-1}$)
$(Rw)_1$	1.6 ± 0.1	1.21 ± 0.01	3.5 ± 0.5	0.4 ± 0.1	7.9 ± 0.1	268 ± 8	142 ± 4
$(Rw)_2$	2.1 ± 0.1	1.02 ± 0.02	2.6 ± 0.3	0.3 ± 0.1	8.5 ± 0.1	245 ± 2	130 ± 2
$(Rw)_3$	0.25 ± 0.01	1.12 ± 0.01	–	0.32 ± 0.03	8.3 ± 0.1	269 ± 1	142 ± 1
$(Rw)_4$	0.30 ± 0.01		–		8.4 ± 0.1	244 ± 3	129 ± 2
$(Rw)_5$	–		–		8.3 ± 0.1	273 ± 6	144 ± 3
$(Rw)_6$	1.0 ± 0.1		3.6 ± 0.2		8.2 ± 0.2	293 ± 3	155 ± 2

$(Rw)_{No}$ means water samples from Rawal dam.

contamination in the water storage tanks. Various parameters for the sediment samples have also been analyzed. The range of Se and Cd if compared with one another would show that Se is lesser in the sediment samples as compared with Cd. In the wastewater samples, the range as shown in Table 3 indicates that water is greatly polluted by Se content rather than by Cd. One important reason could be the effluents that are coming from the domestic sewerage system containing shampoo residues having selenium and also from workshops where both Cd and Se containing compounds are being used. In Table 4, the statistical data for concentration of Cd and Se and of other properties of wastewater samples are provided. These various parameters indicate that this water cannot be used even for irrigation purpose. The range of Cd in the sediment samples taken from the wastewater stream is more than that of Se, therefore, it can safely be stated that under the above conditions of pH and conductance, Cd tends to remain more in the underlying sediments.

3.4. Immobilization of Cd and Se onto Sawaan River sand

Various parameters have been optimized to study this immobilization process.

Table 2
Concentration of the elements found in the water and sediment samples collected from the Nullah Lai, along with the general analysis

Samples	Cd in water (μg·L^{-1})	Cd in sediments (μg·g^{-1})	Se in water (μg·L^{-1})	Se in sediments (μg·g^{-1})	pH	Conductivity (μS·cm^{-1})	TDS (μg·mL^{-1})
$(N)_1$	3.6 ± 0.1	4.1 ± 0.1	4.8 ± 0.1	0.8 ± 0.1	9.1 ± 0.1	458 ± 2	242 ± 1
$(N)_2$		3.1 ± 0.1		0.9 ± 0.1	7.4 ± 0.1	811 ± 13	429 ± 6
$(N)_3$	3.9 ± 0.1	5.2 ± 0.2	4.3 ± 0.1	0.7 ± 0.1	8.5 ± 0.1	686 ± 6	363 ± 4
$(N)_4$		6.0 ± 0.1		1.1 ± 0.1	9.2 ± 0.1	1,100 ± 13	583 ± 7
$(N)_5$	3.3 ± 0.2	5.7 ± 0.1	5.7 ± 0.2	0.8 ± 0.1	9.1 ± 0.2	807 ± 15	409 ± 9
$(N)_6$		7.8 ± 0.1		0.8 ± 0.1	8.8 ± 0.2	474 ± 11	251 ± 6
$(N)_7$	4.1 ± 0.1	5.2 ± 0.1	4.8 ± 0.1	0.9 ± 0.1	8.7 ± 0.2	783 ± 7	415 ± 4
$(N)_8$		3.3 ± 0.1		1.0 ± 0.1	7.2 ± 0.2	1,040 ± 25	551 ± 13
$(N)_9$	4.2 ± 0.2	7.6 ± 0.1	5.8 ± 0.2	0.9 ± 0.1	7.3 ± 0.1	1,066 ± 13	565 ± 7
$(N)_{10}$		7.4 ± 0.1		0.6 ± 0.1	7.5 ± 0.2	1,063 ± 7	564 ± 4

Table 3
Statistical parameters for the concentrations of Cd(II) and Se(IV) and general parameters in various sediment samples collected from the Rawal dam

Parameters	Cd in water (μg·L^{-1})	Cd in sediments (μg·g^{-1})	Se in water (μg·L^{-1})	Se in sediments (μg·g^{-1})	pH	Conductivity (μS·cm^{-1})	TDS (μg·mL^{-1})
Mean	0.74	1.12	1.37	0.35	8.23	269	142
Maximum	2.05 ± 0.1	1.21 ± 0.01	3.6 ± 0.2	0.45 ± 0.07	8.5 ± 0.1	294 ± 6	155 ± 2
Minimum	0.25 ± 0.01	1.02 ± 0.02	0	0.3 ± 0.14	7.9 ± 0.1	244 ± 3	129 ± 2
Range	0.25–2.05	1.02–1.21	0–3.6	0.3–0.45	7.9–8.5	244–294	129–155
Median	0.3	1.11	–	0.32	8.26	269	142
Standard deviation	0.82	0.09	1.74	0.08	0.22	20	10.4

Table 4
Statistical parameters for the concentrations of Cd(II) and Se(IV) and general parameters in various sediment samples collected from the Nullah Lai

Parameters	Cd in water (μg·L^{-1})	Cd in sediments (μg·g^{-1})	Se in water (μg·L^{-1})	Se in sediments (μg·g^{-1})	pH	Conductivity (μS·cm^{-1})	TDS (μg·mL^{-1})
Mean	3.6	4.95	4.8	0.7	8.2	731	385
Maximum	4.2 ± 0.2	7.8 ± 0.1	5.8 ± 0.2	1.1 ± 0.1	9.2 ± 0.1	1,100 ± 13	583 ± 7
Minimum	2.8 ± 0.2	3.1 ± 0.1	4.2 ± 0.2	0.33 ± 0.03	7.2 ± 0.2	436 ± 8	231 ± 4
Range	2.8–4.2	3.1–7.8	4.2–5.8	0.33–1.1	7.2–9.2	436–1,100	231–583
Median	3.6	4.7	4.8	0.8	8.3	734	386
Standard deviation among the samples	0.5	1.7	0.6	0.2	0.7	257	135

3.4.1. Influence of sorptive media and pH

Various sorptive media, HCl, HNO_3 and $HClO_4$ in different concentrations (Table A6) have been used to find out the optimum value of distribution coefficient [15,16]. Not only the sorptive media but also the adsorption system has been checked for pH ranging from 1 to 10. Fig. 1 shows the effect of pH as we move from a more acidic pH to a more basic one. The most suitable sorptive media giving highest values of R_d turns out to be deionized water for Cd(II), however, for Se(IV) it is the solution of pH 4. Therefore in more acidic media, selenium will tend to remain in adsorbed form however greater adsorption of Cd(II) will be observed when the medium is nearly neutral.

3.4.2. Kinetic studies

The kinetic studies are carried out by applying different kinetic equations to the data acquired by observing the effect of shaking time on the distribution coefficient values [16,17]. Fig. 2 demonstrates how the R_d changes with changing shaking time. It can be seen that equilibrium state is quickly reached in case of Cd(II), however, it took quite a while in case of Se(IV). Three kinetic equations have been applied on the data manipulated from the effect of shaking time. Morris–Weber equation for both the elements yields a straight line plot [18] (Fig. 3):

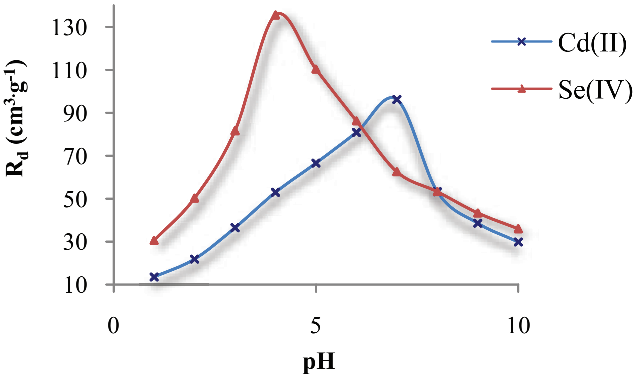

Fig. 1. Effect of pH on the adsorption of Cd(II) and Se(IV).

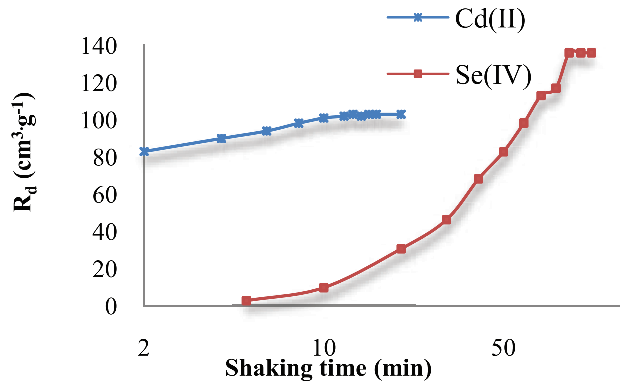

Fig. 2. Effect of shaking time on the adsorption of Cd(II) and Se(IV).

$$q_t = k_d t^{1/2} + \mathrm{I} \tag{2}$$

where q_t stands for the concentration of Se(IV) in solution at some instant, k_d stands for the rate constant of intraparticle diffusion. *I* which refers to the thickness of boundary layer can be explained via the values of intercepts; that is, the larger value of intercept means greater boundary layer effect. The values of k_d for Cd(II) is $(7.16 \pm 0.45) \times 10^{-9}$ cm³ g⁻¹ min⁻¹/² and for Se(IV) is $(3.89 \pm 0.13) \times 10^{-7}$ cm³ g⁻¹ min⁻¹/².

Lagergren rate model (the pseudo-first-order) can be utilized to explain the first-order kinetic model for this process [19]. The equation is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3}$$

In this equation, q_e refers to the Se(IV) concentration at equilibrium, k_1 is the rate constant of the first-order adsorption (min⁻¹). A convenient expression of Lagergren model is plotted in Fig. 4 to find the rate constants. The rate constant for the sorption of Cd(II) and Se(IV) onto the SRs is $(2.13 \pm 0.8) \times 10^{-1}$ min⁻¹ and $(3.75 \pm 0.12) \times 10^{-2}$ min⁻¹, respectively. The above results from the rate constant values also prove that Cd(II) diffuses fast and this diffusion is kinetically more favoured as compared with that of Se(IV). Reichenberg's plot is shown in Fig. 5. Plot of Bt vs. time for both the elements gives straight lines which indicates that film diffusion is not limiting step of the overall adsorption process kinetics [20].

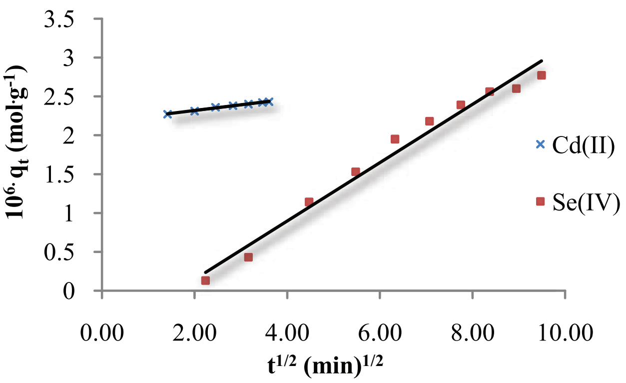

Fig. 3. Morris–Weber plot for Cd(II) and Se(IV) adsorption.

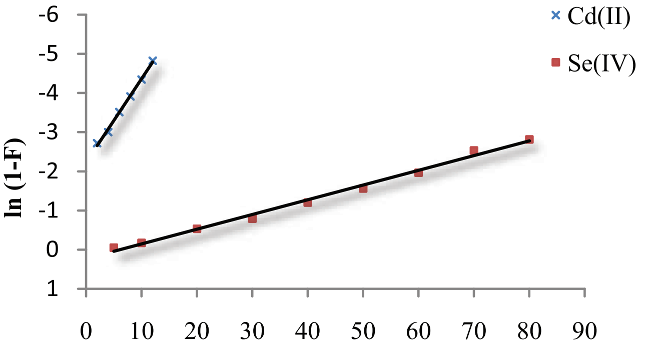

Fig. 4. Lagergren plot for Cd(II) and Se(IV) adsorption.

$$F = (1 - 6/\pi^2)e^{-Bt} \quad (4)$$

or

$$Bt = -0.4977 - \ln(1 - F) \quad (5)$$

3.5. Isotherms

To study various isotherms, the dependence of metal ion's concentration on the R_d has been studied [8,11,15]. The results are shown in Fig. 6. It is observed that R_d decreases with increasing concentrations of both the ions and an extent is reached when there is no further change in its value even if the concentration is enhanced further. Obtaining data from the above graph and manipulating it further, three different isotherms have been drawn. Langmuir isotherm [21] (Fig. 7) can be plotted by using the following straight line equation:

$$C_e/C_{\text{ads}} = 1/M\,b + C_e/M \quad (6)$$

where C_e is the equilibrium concentration of both the elements in the solution, while C_{ads} is the concentration that has been adsorbed on the adsorbent. There are various parameters that can be calculated from the Langmuir's isotherm. M is a constant and can be explained as the maximum amount of solute adsorbed (maximum adsorption at monolayer) while b is a constant related to the binding energy of the solute. The phenomenon of monolayer formation is operative for the sorption of Se(IV) onto the SRs, however, it is not followed so well in the case of Cd(II). $1/M$ which is the moles of adsorption sites per gram giving an indication of the moles of solute adsorbed per gram for the sorption of Se(IV) onto the SRs is (10.38 ± 4.22) × 10^4 mol·g^{-1}, The constant b for the sorption of Se(IV) onto SRs comes out to be (1.94 ± 0.78) × 10^4 L·mol^{-1}. Freundlich isotherm [22] is governed by the following straight line equation (Fig. 8):

$$\log C_{\text{ads}} = \log C_m + 1/n \log C_e \quad (7)$$

There are various parameters evaluated from these plots. The maximum sorption capacity C_m for the sorption of Cd(II) and Se(IV) onto the SRs is calculated to be 0.33 ± 0.1 and 2.83 ± 0.82 mmol·g^{-1}, respectively. $1/n$ is another parameter which tells about the number of active sites in a particular sorbent, and for the sorption of Cd(II) and Se(IV) onto the SRs its value comes out to be 0.47 ± 0.02 and 0.65 ± 0.02, respectively. Dubinin–Radushkevich isotherm [23], often written as DR isotherm is represented by following straight line equation:

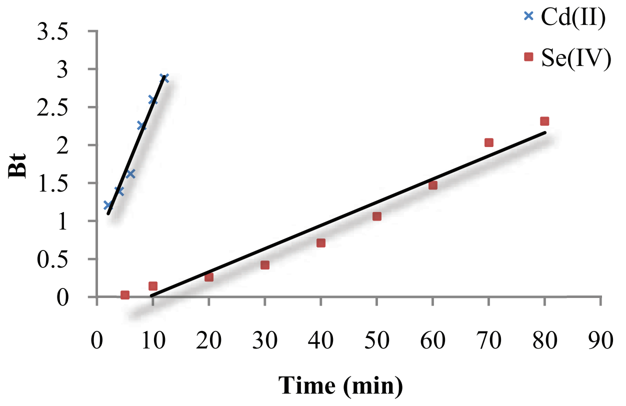

Fig. 5. Reichenberg plot for the sorption Cd(II) and Se(IV).

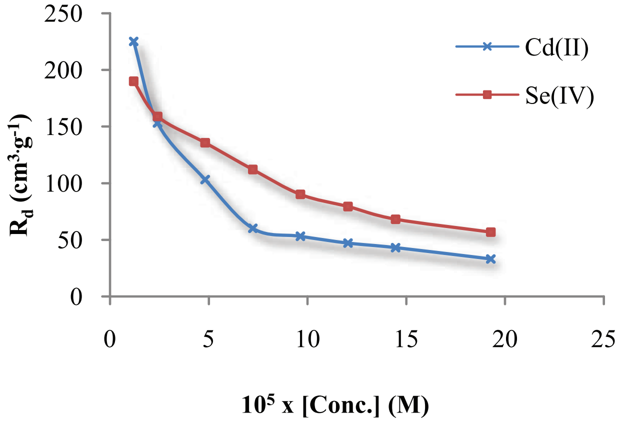

Fig. 6. Dependence of the concentration of Cd(II) and Se(IV) on its adsorption.

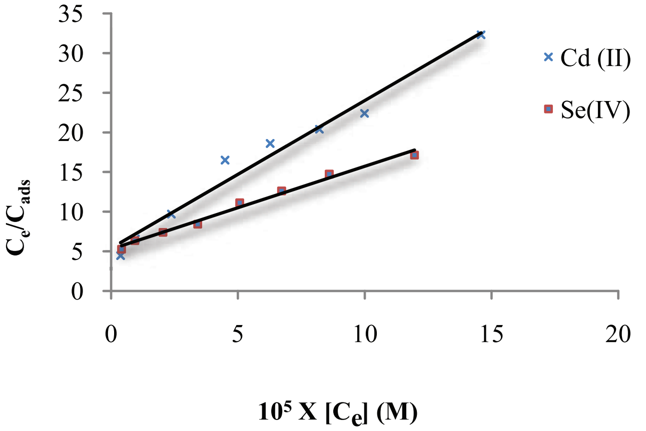

Fig. 7. Langmuir isotherm for the sorption of Cd(II) and Se(IV).

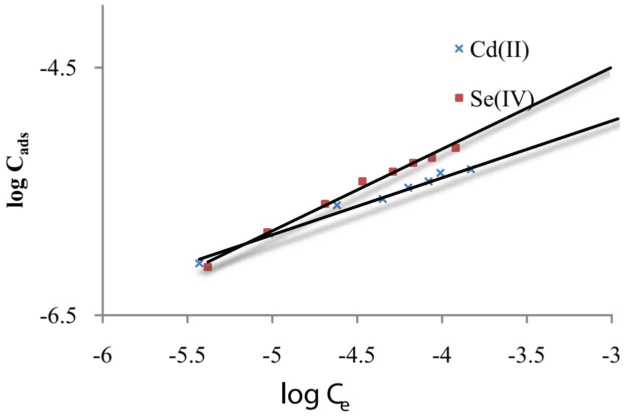

Fig. 8. Freundlich isotherm for the sorption of Cd(II) and Se(IV).

$$\ln C_{\text{ads}} = \ln X_m - \beta\varepsilon^2 \tag{8}$$

The maximum sorption capacity, C_m for the sorption of Cd(II) and Se(IV) onto the SRs is 27.1 ± 2.8 μmol·g^{-1} and 0.1052 ± 0.01433 mmol·g^{-1}, respectively (Fig. 9).

An important aspect of DR isotherm is the evaluation of Polannyi adsorption potential and sorption energy which are, respectively, given by:

$$\varepsilon = RT\ln(1 + 1/C_{eq}) \tag{9}$$

$$E = 1/\sqrt{-2\beta} \tag{10}$$

The Polannyi constant β and sorption energy E for the sorption of Cd(II) is (–0.0036 ± 0.0001) kJ^2·mol^{-2} and 11.80 ± 0.25 kJ·mol^{-1} while the sorption of Se(IV) is (–0.0063 ± 0.0001) kJ^2·mol^{-2} and 8.93 ± 0.04 kJ·mol^{-1}, respectively. The sorption energies in both the cases are indicative of chemisorption.

3.6. Thermodynamic parameters

The thermodynamic parameters can be studied by applying the following straight line equation [8,16] (Fig. 10):

$$\log K_c = -\Delta H/2.303RT + \Delta S/2.303R \tag{11}$$

The change in free energy (ΔG) is given at individual temperatures; however, change in enthalpy (ΔH) can be calculated from the slope of the straight line, and change in

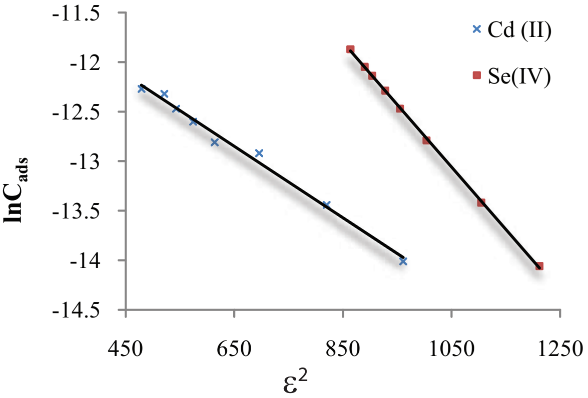

Fig. 9. Dubinin–Radushkevich isotherm.

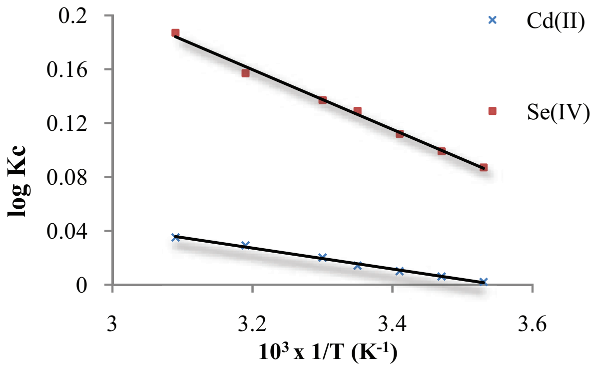

Fig. 10. Temperature dependence of the sorption process.

Table 5
Effect of various ions (commonly present in water) on R_d for the sorption of Cd(II) and Se(IV) onto Sawaan River sand

Added ion under consideration	R_d (cm^3·g^{-1})	
	Cd(II)	Se(IV)
None (optimum condition)	103 ± 1 (13 min)	103 ± 1 (13 min)
Sodium (Na^+)	105 ± 1	105 ± 1
Potassium (K^+)	101 ± 1	101 ± 1
Zinc (Zn^{2+})	95 ± 1	95 ± 1
Copper (Cu^{2+})	359 ± 2	359 ± 2
Magnesium (Mg^{2+})	288 ± 1	288 ± 1
Calcium (Ca^{2+})	353 ± 2	353 ± 2
Lead (Pb^{2+})	187 ± 1	187 ± 1
Chromium (Cr^{3+})	214 ± 1	214 ± 1
Uranium (U^{3+})	145 ± 1	145 ± 1
Selenium (Se^{4+})	93 ± 1	93 ± 1
Nitrate (NO_3^-)	104 ± 1	104 ± 1
Bicarbonate (HCO_3^-)	277 ± 2	277 ± 2
Chloride (Cl^-)	489 ± 3	489 ± 3
Bromide (Br^-)	326 ± 3	326 ± 3
Iodide (I^-)	235 ± 2	235 ± 2
Carbonate (CO_3^{2-})	118 ± 3	118 ± 3
Sulphate (SO_4^{2-})	112 ± 2	112 ± 2
Oxalate ($C_2O_4^{2-}$)	157 ± 1	157 ± 1
Sulphide (S^{2-})	237 ± 2	237 ± 2

entropy (ΔS) from the intercept. ΔH for Cd(II) and Se(IV) sorption onto the SRs is 1.49 ± 0.18 and 4.24 ± 0.17 kJ·mol^{-1}, respectively. ΔS for the sorption of Cd(II) onto the SRs is 5.29 ± 0.19 J·mol^{-1}·K^{-1}, ΔS for the sorption of Se(IV) sorption is 16.6 ± 0.6 J·mol^{-1} K^{-1}, ΔG_{298} for the sorption of Cd(II) is –0.073 ± 0.007 kJ·mol^{-1} and ΔG_{298} for the sorption of Se(IV) is –0.73 ± 0.03 kJ·mol^{-1}.

3.7. Effect of various ions

From Table 5 it can be seen that in the case of Cd(II), the presence of HCO_3^-, Cl^-, Br^-, I^- and S^{2-} among the anions and Cu^{2+}, Mg^{2+}, Ca^{2+}, Pb^{2+} and Cr^{3+} among the cations enhance the sorption by elevating the value of R_d. Pb(II) and Cd(II) tend to suppress the sorption by lowering the R_d values. While among the anions $(HCO_3)^{1-}$, $(CO_3)^{1-}$ and oxalate tend to decrease the adsorption because more stable anionic complexes of Se(IV) are formed having low sorption affinity towards the sorbent. One of the various possibilities could be that these anionic complexes may not have any affinity towards the adsorbent surface giving negligible adsorption thus reducing the sorption of Se(IV) in their presence. Rest all the other cations and anions tend to enhance the sorption by increasing the R_d.

4. Conclusions

As discussed in the introduction section, the elements tend to remain in the underlying sediments more than the water column above them unless there is a greater variation in the physical parameters of the water and sediments' environment. The mean value of Cd in drinking water samples is 0.74 μg·L^{-1} and that for Se is 1.37 μg·L^{-1}. Mean value of Cd and Se concentration in wastewater samples are 3.6 and 4.8 μg·L^{-1} while range of these elements is 2.8–4.2 and 4.2–5.8 μg·L^{-1}, respectively. Mean value of Cd and Se concentration in sediment samples taken from Rawal dam are 1.12 and 0.35 μg·g^{-1}, respectively, while in Nullah Lai are 4.95 and 0.7 μg·g^{-1}, respectively. The sorption energy E for the sorption of Cd(II) is 11.80 ± 0.25 kJ·mol^{-1} while the sorption of Se(IV) is 8.93 ± 0.04 kJ·mol^{-1}. The results of kinetic and thermodynamic data show that sands can effectively be used as adsorbents for removal of toxic elements from water.

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Annexure

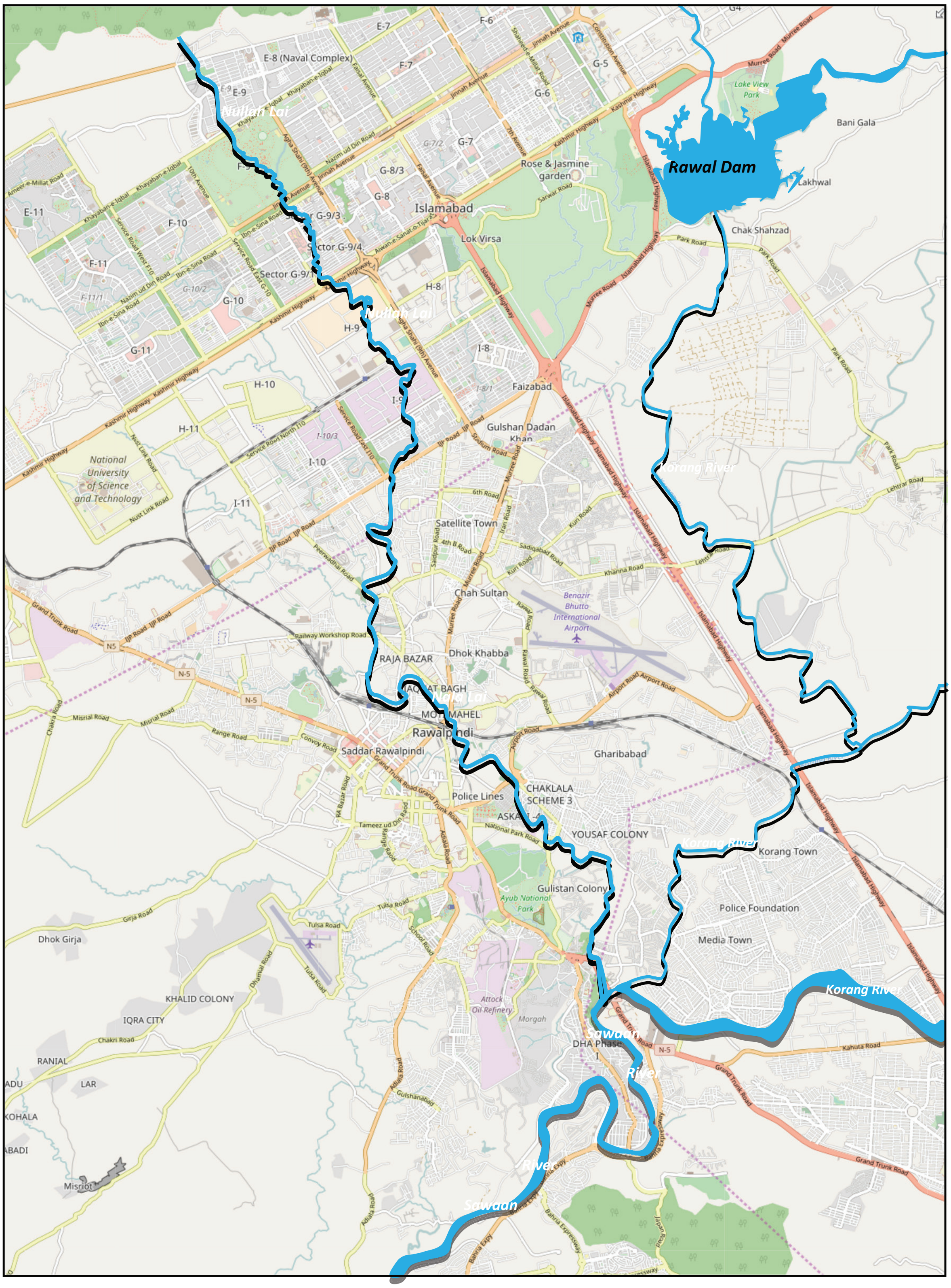

Fig. A1. Location of Rawal dam, Nullah Lai and Sawaan River.

Table A1
Comparison of the actual and measured amounts of the elements in the standard reference materials employing various techniques

Description	Cadmium ($mg{\cdot}g^{-1}$)	Selenium ($mg{\cdot}g^{-1}$)
Actual values in NBS-1645	10.2 ± 0.5	1.2 ± 0.3
Measured values by DPASV in NBS-1645	10.5 ± 0.9	1.1 ± 0.2
Measured values by AAS in NBS-1645	10.4 ± 1.1	Not measured
Actual values in IAEA soil sample-1	0.26 ± 0.05	2.9 ± 1.6
Measured values by AAS in IAEA soil sample-1	0.27 ± 0.05	2.6 ± 0.5

Table A2
Locations at Rawal dam from where water and sediment samples were collected

Symbol of sample	Location
$(S.R)_1$[a]	Bani Gala
$(S.R)_2$[a]	From the bank
$(S.R)_3$[a]	About 10 feet away from the bank
$(S.R)_4$	Taken from one-fourth of the total distance of Rawal dam from the bank width wise
$(S.R)_5$	Taken from half of the total distance of Rawal dam from bank width wise
$(S.R)_6$	Inlet pool from where water goes to the filtration plant
$(S.R)_7$	Outlet pool from where filtered/processed water is supplied to various parts of Islamabad, Rawalpindi

[a] Places from where sediment samples were also collected.

Table A3
Locations at the Nullah Lai and from where water and sediment samples were collected

Symbol of sample[a]	Locations at Nullah Lai (L) from where samples were collected
$(N)_1$	Aabpara
$(N)_2$	Zero point
$(N)_3$	G-10/4
$(N)_4$	Peervadhai
$(N)_5$	I-10
$(N)_6$	Pindora
$(N)_7$	Kachi Basti
$(N)_8$	Mareer (L)
$(N)_9$	Scheme-3, bridge
$(N)_{10}$	Scheme-3, near residential area

[a] Water samples were only collected from the odd number places.

Table A4
Effect of various digestion matrices on the measured amounts of Cd(II) and Se(IV) in the sediment sample N_4 and N_6 taken from the Nullah Lai

Elements	Concentration ($\mu g{\cdot}g^{-1}$) of the element in different digestion matrices		
	$HNO_3 + HClO_4$	$HNO_3 + HClO_4 + H_2O_2$	$HNO_3 + HCl$
Cadmium (N_4)	7.2 ± 0.1	7.8 ± 0.1	7.5 ± 0.6
Cadmium (N_6)	6.2 ± 0.1	6.1 ± 0.1	5.9 ± 0.1
Selenium (N_4)	0.6 ± 0.1	0.8 ± 0.1	0.6 ± 0.1
Selenium (N_6)	0.9 ± 0.1	1.1 ± 0.1	0.6 ± 0.1

Table A5
Recovery study of Cd(II) and Se(IV) from the water samples $(S.R)_2$ and $(S.R)_3$ of the Rawal dam after adding known amounts of the given element

Sample	Cd (μg·L^{-1})	Se (μg·L^{-1})
$(S.R)_2$	2.1 ± 0.1	2.6 ± 0.3
$(S.R)_2$ + 10 (μg L^{-1})	12.25 ± 0.1	12.8 ± 0.5
$(S.R)_2$ + 20 (μg L^{-1})	22.4 ± 0.2	23.2 ± 0.4
$(S.R)_3$	0.25 ± 0.05	–
$(S.R)_3$ + 10 (μg L^{-1})	10.4 ± 0.3	10.1 ± 0.1
$(S.R)_3$ + 20 (μg L^{-1})	20.6 ± 0.5	19.9 ± 0.4

Table A6
Effect of different concentrations of various sorptive media on the adsorption of Cd(II) and Se(IV)

Sorptive medium	Concentration of sorptive medium (M)	R_d (cm^3 g^{-1})	
		Cd(II)	Se(IV)
HCl	0.001	97 ± 1	65.3 ± 0.4
	0.01	88 ± 1	51.8 ± 0.2
	0.1	70 ± 1	43.5 ± 0.1
HNO_3	0.001	88 ± 1	108 ± 1
	0.01	68 ± 2	86 ± 1
	0.1	35 ± 1	78.5 ± 0.2
$HClO_4$	0.001	99 ± 1	116 ± 1
	0.01	89 ± 1	101.3 ± 0.4
	0.1	66 ± 1	85.6 ± 0.3
Deionized water	–	103 ± 1	98.5 ± 0.6