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# Adsorption of heavy metals from multi-metal aqueous solution by sunflower plant biomass-based carbons

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**Abstract** This study reports the competitive adsorption of Ni(II), Cd(II) and Cr(VI) onto sunflower waste biomass carbons, viz. sunflower head carbon and sunflower stem carbon from multi-metal aqueous solution. The adsorption capacity of the adsorbents was highest in mono-metal system but decreased with increase in the number of co-ions. The adsorption capacity in mono-metal system was 0.32 and 0.45 mM/g for Ni(II), 0.25 and 0.32 mM/g for Cd(II) and 0.20 and 0.28 for Cr(VI) by sunflower head carbon and sunflower stem carbon, respectively, whereas, in a binary system, adsorption capacity of sunflower head carbon for Ni(II) was 0.24 mM/g in 0.5 mM Cd(II) solution which was further reduced to 0.18 mM/g in 2.0 mM Cd(II). The effect of co-cations was more pronounced in tertiary systems. Similar behavior was observed for other systems also. The interactive effect of multi-metal ions in binary and tertiary component systems was antagonistic in nature, i.e., the effect of mixture is less than the sum of individual effect of the constituents or when the effect of individual substances added together is less than the expected in response to multiple substances. Langmuir model best fitted the data for all the systems with $r^2$ value >0.95.

**Keywords** Competitive adsorption · Chromium · Cadmium · Nickel · *Helianthus annuus*

## Introduction

Various industrial processes generate metal-laden wastewaters. The multiple components of wastewaters cause interactive effects depending on several factors such as number of co-cations competing for binding sites, metal concentration, equilibrium concentration of metal ion species, pH, nature and quantity of the adsorbent biomass (Saeed et al. 2005). Treatment of such wastewaters is a challenge for environmental engineers, municipalities and policy makers. Several technologies are available for the treatment of heavy metals containing wastewaters. Among them, chemical precipitation, reverse osmosis, oxidation–reduction, electrodialysis, solvent extraction and adsorption are common. But adsorption is the most sought out technology for such kind of waters which contains trace amount of heavy metals and that cannot be removed by other methods. Adsorption can be applied for treatment of wastewater using various materials like agricultural waste, algae, bacteria, fungi, zeolites, clay, mud and fly ash as adsorbent.

A large volume of work on the adsorption of heavy metal ions from mono-metal solutions by various adsorbents is available in literatures (Vinh et al. 2015; Reddy et al. 2015; Ghasemi et al. 2014; Mahajan and Sud 2013; Machida et al. 2006; Kadirvelu et al. 2004; Li et al. 2003; Nguyen et al. 2013). Multi-metal adsorption studies are

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important to assess the level of interference caused by co-ions present in the wastewater and the efficiency of adsorbent to remove those ions from wastewaters (Srivastva et al. 2006). Competitive adsorption of various heavy metals in multi-metal system has been reported in yesteryears only by a few workers. Hadi et al. (2014) reported the adsorption of Cu, Pb and Zn from single, binary and ternary system using e-waste-based adsorbent. Mohan and Singh (2002) found that adsorption capacity of activated carbon for Cd(II) and Zn(II) decreased in multi-metal system as compared to binary system. Chiban et al. (2011) reported that adsorption capacity of Pb(II) by dried *Carpobrothus edulis* decreased in the presence of Cd(II) in binary system. Ting and Teo (1994) reported that in multi-component system, metal ions interact with each other in synergistic, antagonistic or non-interactive manner and the results cannot be predicted on the basis of single metal studies. Therefore, it is worthwhile to study the simultaneous adsorption of two or more metals and also to quantify the interference of a metal with the adsorption of other.

Plant biomass is composed of biopolymers, mainly containing lignocellulose and tannins which may lead to binding of metal ions due to the presence of functional groups like hydroxyl, carboxyl, carbonyl, thiol and amine (Witek-Krowiak 2012). In the present study, sunflower waste biomass was chosen as the prospective precursor for preparation of adsorbents. Sunflower is one of the five largest oil producing crops in the world and is known for edible oil and bioethanol production. After extraction of oil, huge quantities of sunflower heads and stalks are generated that do not find any suitable end use and are burnt in the fields causing environmental pollution (Sharma et al. 2012).

The sunflower waste biomass also contains functional groups like hydroxyl, carboxyl and carbonyl as indicated by FT-IR analysis reported elsewhere (Jain et al. 2010). The adsorbents prepared from this biomass had good adsorption potential for Cr(VI), Ni(II) and Cd(II) from mono-metal systems (Jain et al. 2009, 2013, 2014). Yet, no data are available on the usage of sunflower waste biomass for the removal of heavy metals from multi-metal system.

So, in continuation of our earlier work, this study reports the performance of two adsorbents, viz. sunflower head carbon (SHC) and sunflower stem carbon (SSC) for the removal of metals from multi-metal aqueous systems. In this study, the metals of interest were chromium, nickel and cadmium, which are commonly encountered in many of the industrial effluents.

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## Materials and methods

### Adsorbents

Two adsorbents were prepared from deseeded heads and stems of sunflower (*Helianthus annuus)* waste biomass, viz. sunflower head carbon (SHC) and sunflower stem carbon (SSC) as reported by Jain et al. (2010). A brief description of the preparation of adsorbents has been given here. The sunflower heads and stems (*H. annuus*) were collected directly from the agricultural fields. They were ground separately into fine powder and were mixed with concentrated $H_2SO_4$ in the ratio of 2:1 ($H_2SO_4$: sunflower, v/w) and carbonized at 150 °C in hot air oven for 24 h. The charred material was repeatedly washed with deionized water until excess acid was removed and finally soaked in 2 % $Na_2HCO_3$ (w/v) overnight to remove any residual acid from the material. The adsorbent was washed again with deionized water several times and dried in hot air oven at 105 °C for 8 h. The adsorbent obtained was sieved from standard sieve (ASTM No. 50, I.S.S. No. 30) to get the particle size of ≤300 μm. The adsorbent was designated as sunflower head carbon (SHC) and sunflower stem carbon (SSC).

The surface characterization of the adsorbents was done using SEM, EDX, FT-IR and BET surface area as reported elsewhere (Jain et al. 2010), while the physico-chemical parameters were found to be pH = 3.7 and 4.1, ash content = 4.2 and 3.8 %, moisture content = 2.5 and 2.8 %, bulk density = 0.8 and 0.6 g cc$^{-1}$, water soluble matter = 2.3 and 1.8 %, acid soluble matter = 10.3 and 8.3 %, elemental analysis = C—51 and 41 %, H—3.1 and 2.8 %, N—0 and 8.5 %, O—45.9 and 44.7 % for SHC and SSC, respectively. Among SHC and SSC, SSC proved to be the better adsorbent due to high surface area and adsorption capacity. This can be explained on the basis of structure of sunflower stems. The sunflower stems are made of an outer covering called skin and an inner soft tissue called pith. Skin is a fibrous and cellulose-based structure, while pith is soft, spongy and porous (Sun and Xu 1997). Sun and Xu (1997) also revealed that the BET surface area of sunflower skin is 1.11 and that of pith is 2.31 m$^2$/g. But when total area of both skin and pith is considered, then it decreases to 1.20 m$^2$/g. The results from our previous study are in agreement with Sun and Xu showing that the BET surface area of SHC was 1.17 and that of SSC was 1.28 m$^2$/g (Jain et al. 2010).

### Batch studies

#### Mono-component study

Batch mode adsorption studies of Ni(II), Cd(II) and Cr(VI) by SHC and SSC were performed to determine their

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adsorption capacity in mono-component system. Fifty milliliters of metal ion solution of concentration = 1.0 mM with an adsorbent dose of 0.2 g/50 mL was agitated at a temperature of 25 ± 1 °C in an orbital shaker for 180 min at 180 rpm. All the experiments were carried out at an optimum pH of 2.0 for Cr(VI), 6.0 for Cd(II) and Ni(II) based on our earlier findings (Jain et al. 2010, 2013, 2014). The metal uptake loading capacity $q_e$ (mM of metal per g of adsorbent) for each sorption system was determined using Eq. 1:

$$q_e(\text{mM/g}) = \left[\frac{C_i - C_e}{M}\right] \times V \tag{1}$$

where $C_i$ and $C_e$ are the initial and equilibrium concentration, $V$ is the volume of the solution in (L) and $M$ is the mass of the adsorbent (g). Metal solutions were prepared using potassium dichromate ($K_2Cr_2O_7$), nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] and cadmium sulfate ($3CdSO_4 \cdot 8H_2O$). Residual metal ion concentration in the solution was determined using atomic absorption spectrophotometer (Shimadzu AA 6300, Japan).

### Multi-component study

The effect of co-cations on the adsorption of Ni(II), Cd(II) and Cr(VI) by SHC and SSC was studied in binary and tertiary component systems. Experimental design used in the study consisted of binary system, viz. Ni(II) + Cd(II), Ni(II) + Cr(VI), Cd(II) + Ni(II), Cd(II) + Cr(VI), Cr(VI) + Ni(II), Cr(VI) + Cd(II) and tertiary system, viz. Ni(II) + Cr(VI) + Cd(II), Cd(II) + Cr(VI) + Ni(II), Cr(VI) + Ni(II) + Cd(II).

The effect of co-cations on Ni(II), Cd(II) and Cr(VI) adsorption capacity has been studied at different co-cation concentrations. For binary and tertiary component system, the metal and co-cation concentrations (mM) were maintained at a ratio of 1:1 and 1:1:1. Adsorption studies were carried out by keeping the concentration of first metal constant and varying the concentration of other metal(s) ions at optimum pH of the former metal ion obtained in case of single metal system. The process parameters optimized for mono-metal solutions were applied for binary and tertiary systems, viz. pH 2.0 for Cr(VI) and 6.0 for Ni(II) and Cd(II), volume = 50 mL, co-cation concentration varied between 0.5 mM and 2.0 mM for binary system and between 0.25:0.25 and 1.0:1.0 for tertiary system, adsorbent dose = 0.2 g/ 50 mL, contact time = 180 min, stirring speed = 180 rpm and temperature = 25 ± 1 °C (Jain et al. 2010).

### Adsorption isotherms

Adsorption data were modeled using Langmuir and Freundlich equations. These models are given below in Eqs. 2 and 3:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{2}$$

$$\log_{10} q_e = \log_{10}(K_f) + \left(\frac{1}{n}\right) \log_{10}(C_e) \tag{3}$$

where $C_e$ is the equilibrium concentration of metal ion (mM/L), $q_e$ is the amount of metal adsorbed (mM/g), $Q_o$ is Langmuir maximum adsorption capacity (mM/g), $b$ is the constant related to free energy of adsorption (L/mM), $K_f$ is the Freundlich relative adsorption capacity (mM/g) and $n$ is the intensity of the adsorbent.

## Results and discussion

It was evident from the results that adsorption capacity of Ni(II), Cd(II) and Cr(VI) by SHC and SSC in mono-metal system was higher than multi-metal systems. Among the two adsorbents, SSC had higher adsorption capacity than SHC for Ni(II), Cd(II) and Cr(VI) in mono-component system. It was 0.32, 0.25 and 0.20 mM/g for Ni(II), Cd(II) and Cr(VI), respectively, by SHC, whereas 0.45, 0.32 and 0.28 mM/g for Ni(II), Cd(II) and Cr(VI), respectively, by SSC (Figs. 1a, 2a, 3a). This variation may be due to the fact that SSC was prepared from sunflower stem which is more porous due to the presence of pith in it and has higher surface area than sunflower heads. The order of adsorption capacity in mono-component system by SHC and SSC was Ni(II) > Cd(II) > Cr(VI).

### Nickel adsorption in multi-metal system (binary and tertiary system)

The effect of various co-cations on the adsorption capacity of SHC and SSC in binary and tertiary system for Ni(II) has been depicted in Fig. 1a, b. The results showed that as the concentration of the co-cations was increased from 0.5 to 2.0 mM in the solution, the adsorption capacity of the adsorbents for Ni(II) decreased. The adsorption capacity of SHC decreased from 0.24 mM/g to 0.18 mM/g and that of SSC from 0.27 mM/g to 0.21 mM/g for Ni(II) in Ni(II) + Cd(II) binary system (Fig. 1a). The adsorption capacity of SHC decreased from 0.20 mM/g to 0.14 mM/g and that of SSC from 0.22 mM/g to 0.16 mM/g for Ni(II) in Ni(II) + Cr(VI) binary system (Fig. 1a).
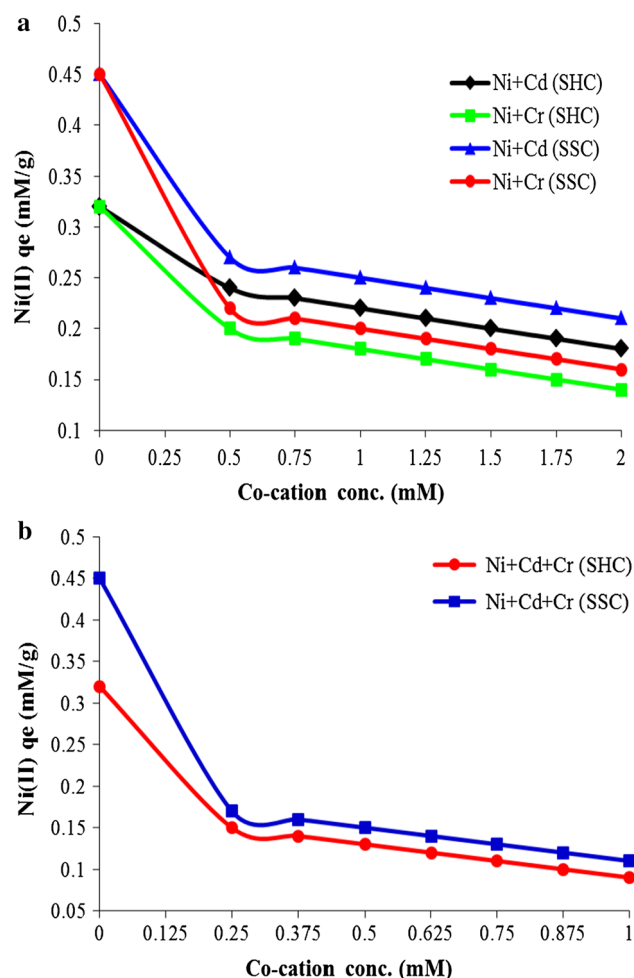
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**Fig. 1** **a** Effect of co-cation conc. on Ni(II) sorption by SHC and SSC in binary system at Ni(II) conc. = 1.0 mM, pH = 6.0, dose = 4.0 g/L, contact time = 180 min, stirring speed = 180 rpm, temp. = 25 ± 1 °C. **b** Effect of co-cation conc. on Ni(II) sorption by SHC and SSC in tertiary system at Ni(II) conc. = 1.0 mM, pH = 6.0, dose = 4.0 g/L, contact time = 180 min, stirring speed = 180 rpm, temp. = 25 ± 1 °C

**Fig. 2** **a** Effect of co-cation conc. on Cd(II) sorption by SHC and SSC in binary system at Cd(II) conc. = 1.0 mM, pH = 6.0, dose = 4.0 g/L, contact time = 180 min, stirring speed = 180 rpm, temp. = 25 ± 1 °C. **b** Effect of co-cations conc. on Cd(II) sorption by SHC and SSC in tertiary system at Cd(II) conc. = 1.0 mM, pH = 6.0, dose = 4.0 g/L, contact time = 180 min, stirring speed = 180 rpm, temp. = 25 ± 1 °C

The adsorption capacity of SHC decreased from 0.15 mM/g to 0.09 mM/g and that of SSC decreased from 0.17 mM/g to 0.11 mM/g in Ni(II) + Cd(II) + Cr(VI) tertiary system (Fig. 1b). The adsorption capacity was minimum at 2.0 mM concentration in all the three systems, i.e., Ni(II) + Cd(II), Ni(II) + Cr(VI) and Ni(II) + Cd(II) + Cr(VI), whereas the adsorption capacity of Ni(II) was highest, i.e., 0.32 mM/g by SHC and 0.45 mM/g by SSC at 1.0 mM Ni(II) concentration in mono-metal system (Fig. 1a, b).

**Cadmium adsorption in multi-metal system (binary and tertiary system)**

The effect of various co-cations on the adsorption capacity of SHC and SSC in binary and tertiary system for Cd(II)
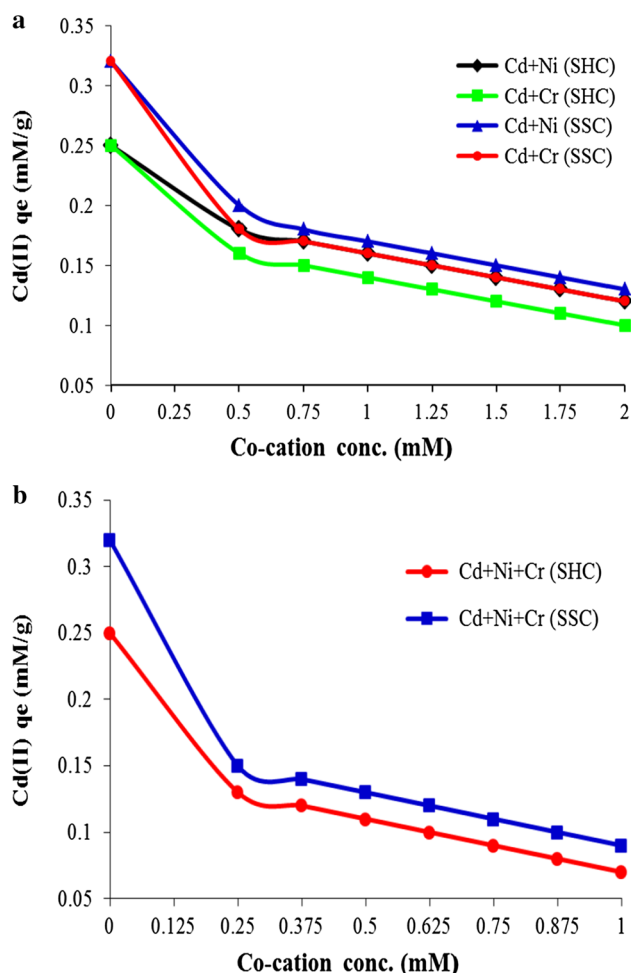
adsorption is depicted in Fig. 2a, b. The adsorption capacity of SHC for Cd(II) decreased from 0.18 mM/g to 0.12 mM/g and that of SSC decreased from 0.20 mM/g to 0.13 mM/g in Cd(II) + Ni(II) binary system as the concentration of the co-cation increased in the solution from 0.5 to 2.0 mM (Fig. 2a). The adsorption capacity of SHC decreased from 0.16 mM/g to 0.10 mM/g and that of SSC decreased from 0.18 mM/g to 0.12 mM/g for Cd(II) in Cd(II) + Cr(VI) binary system (Fig. 2a).

The adsorption capacity of SHC for Cd(II) decreased from 0.13 mM/g to 0.07 mM/g and that of SSC decreased from 0.15 mM/g to 0.09 mM/g in Cd(II) + Ni(II) + Cr(VI) in tertiary system (Fig. 2b). The adsorption capacity was minimum at 2.0 mM concentration in all the three systems that are Cd(II) + Ni(II), Cd(II) + Cr(VI) and Cd(II) + Ni(II) + Cr(VI).
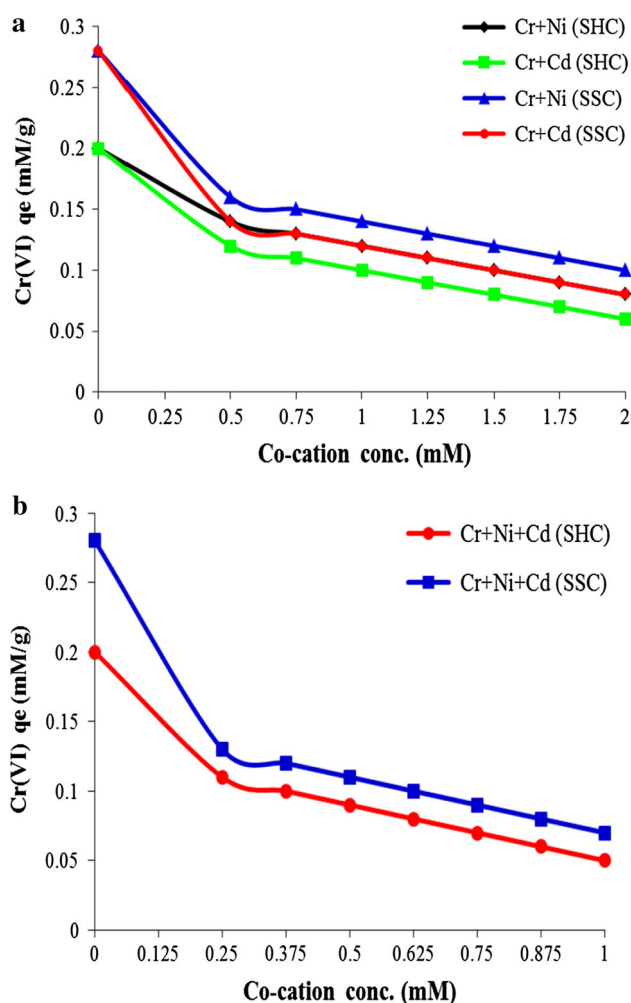
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**Fig. 3 a** Effect of co-cation conc. on Cr(VI) sorption by SHC and SSC in binary system at Cr(VI) conc. = 1.0 mM, pH = 2.0, dose = 4.0 g/L, contact time = 180 min, stirring speed = 180 rpm, temp. = 25 ± 1 °C. **b** Effect of co-cations conc. on Cr(VI) sorption by SHC and SSC in tertiary system at Cr(VI) conc. = 1.0 mM, pH = 2.0, dose = 4.0 g/L, contact time = 180 min, stirring speed = 180 rpm, temp. = 25 ± 1 °C

## Chromium adsorption in multi-metal system (binary and tertiary system)

The effect of various co-cations on the adsorption capacity of SHC and SSC for Cr(VI) in binary and tertiary system is depicted in Fig. 3a, b. As the concentration of the co-cations was increased in the solution from 0.5 to 2.0 mM, the adsorption capacity of the studied adsorbents for Cr(VI) decreased. The adsorption capacity of SHC decreased from 0.14 mM/g to 0.08 mM/g and that of SSC decreased from 0.16 mM/g to 0.10 mM/g for Cr(VI) in Cr(VI) + Ni(II) binary system (Fig. 3a). The adsorption capacity of SHC decreased from 0.12 mM/g to 0.06 mM/g and that of SSC decreased from 0.14 mM/g to 0.08 mM/g for Cr(VI) in Cr(VI) + Cd(II) binary system (Fig. 3a). The adsorption capacity of SHC for Cr(VI) decreased from 0.11 mM/g to 0.05 mM/g and that of SSC decreased from 0.13 mM/g to 0.07 mM/g in Cr(VI) + Ni(II) + Cd(II) tertiary system (Fig. 3b).

It is evident from the results that co-adsorption resulted in lowering of the adsorption capacity for a particular ion. The results also indicated that the co-cations in the system competed with Ni(II), Cd(II) and Cr(VI) for adsorption sites. Relatively less adsorption capacity in binary and tertiary component system may be due to the competition among different metal ions for the available binding sites on the adsorbents (Aksu et al. 1999). de Carvalho et al. (1995) reported that decrease in adsorption capacity in the presence of co-ions may be due to the progressive interference of ions because of overlapping on sorption sites at higher concentration. Factors that affect the adsorption preference of an adsorbent for metals in multi-metal system are related to the physico-chemical properties of the solution such as pH, temperature surface properties of the adsorbent and the properties of the metals such as electronic configuration, electronegativity and ionic radius (Srivastava et al. 2006).

**Table 1** Ionic properties of studied metal ions

| Property | Cr(VI) | Ni(II) | Cd(II) |
|---|---|---|---|
| Atomic weight | 51.01 | 58.69 | 112.41 |
| Molecular weight | 294.18 | 290.81 | 769.52 |
| Electronic configuration | $[Ar]3d^5 4s^1$ | $[Ar]3d^8 4s^2$ | $[Kr]4d^{10} 5s^2$ |
| Electronegativity | 1.66 | 1.91 | 1.69 |
| Ionic radii (A°) | 0.52 | 0.72 | 0.95 |
| Hydrated radii (A°) | 4.61 | 4.04 | 4.26 |
| Coordination number | 6 & 4 | 4 | 6 & 4 |
| Standard Reduction Pot. (V) | $Cr^{6+} + 3e^- \rightarrow Cr^{3+}(1.1)$ $Cr^{3+} 3e^- \rightarrow Cr (-0.74)$ | $Ni^{2+} + 2e^- \rightarrow Ni (-0.25)$ | $Cd^{2+} + 2e^- \rightarrow Cd (-0.403)$ |

*Source* (Kadirvelu et al. 2008)

**Table 2** Interactive effect of a mixture of metal ions in binary and tertiary systems

| Metal system | SHC | | SSC | |
|---|---|---|---|---|
| | $R_i$ (%) | Interactive effect | $R_i$ (%) | Interactive effect |
| Nickel | | | | |
| Ni(II) + Cd(II) | 68.8 | Antagonistic | 57.8 | Antagonistic |
| Ni(II) + Cr(VI) | 56.3 | Antagonistic | 44.4 | Antagonistic |
| Ni(II) + Cd(II) + Cr(VI) | 28.1 | Antagonistic | 24.4 | Antagonistic |
| Cadmium | | | | |
| Cd(II) + Ni(II) | 64.0 | Antagonistic | 53.0 | Antagonistic |
| Cd(II) + Cr(VI) | 56.0 | Antagonistic | 50.0 | Antagonistic |
| Cd(II) + Ni(II) + Cr(VI) | 28.0 | Antagonistic | 28.1 | Antagonistic |
| Chromium | | | | |
| Cr(VI) + Ni(II) | 60.0 | Antagonistic | 50.0 | Antagonistic |
| Cr(VI) + Cd(II) | 50.0 | Antagonistic | 42.9 | Antagonistic |
| Cr(VI) + Ni(II) + Cd(II) | 25.0 | Antagonistic | 25.0 | Antagonistic |

$R_i$ Relative adsorption capacity

**Table 3** Langmuir and Freundlich parameters for Ni(II), Cd(II) and Cr(VI) in mono, binary and tertiary system by SHC

| Metal Combinations | SHC | | | | | |
|---|---|---|---|---|---|---|
| | Langmuir | | | Freundlich | | |
| | $Q_o$ | $b$ | $r^2$ | $K_f$ | $n$ | $r^2$ |
| Mono-component | | | | | | |
| Ni(II) | 0.26 | 0.2 | 0.9967 | 0.21 | 1.7 | 0.7654 |
| Cd(II) | 0.20 | 0.4 | 0.9985 | 0.17 | 2.1 | 0.8281 |
| Cr(VI) | 0.18 | 0.6 | 0.9932 | 0.14 | 1.9 | 0.8712 |
| Binary component | | | | | | |
| Ni(II) + Cd(II) | 0.15 | −5.1 | 0.9896 | 0.15 | 0.5 | 0.8599 |
| Ni(II) + Cr(VI) | 0.11 | −10.2 | 0.9894 | 0.10 | 2.2 | 0.9734 |
| Cd(II) + Ni(II) | 0.09 | −6.4 | 0.9864 | 0.08 | 1.5 | 0.9785 |
| Cd(II) + Cr(VI) | 0.06 | −4.4 | 0.9817 | 0.06 | 1.1 | 0.9803 |
| Cr(VI) + Ni(II) | 0.04 | −3.2 | 0.9742 | 0.05 | 0.8 | 0.9798 |
| Cr(VI) + Cd(II) | 0.02 | −2.2 | 0.8539 | 1.3 | 0.2 | 0.4378 |
| Tertiary component | | | | | | |
| Ni(II) + Cd(II) + Cr(VI) | 0.05 | −3.7 | 0.9808 | 0.06 | 0.9 | 0.9785 |
| Cd(II) + Ni(II) + Cr(VI) | 0.03 | −2.8 | 0.9685 | 0.4 | 0.5 | 0.147 |
| Cr(VI) + Ni(II) + Cd(II) | 0.02 | −2.1 | 0.9494 | 0.3 | 0.5 | 0.0667 |

The mechanism of adsorption in multi-metal system can be predicted on the basis of ionic properties of the metal ions. The results signify that Ni(II) is the most adsorbed ion among the three studied metal ions due to more accessibility to the pores as it has the smallest hydrated radii as compared to other two ions (Table 1). Also, it has the highest standard reduction potential (Table 1) which implies that metals with higher standard reduction potential tend to exhibit a stronger ionic interaction with an electron-rich surface of the adsorbents (Mohan and Singh 2002). Further, it is the most electronegative ion among the three, so it is more strongly attracted to the surface of the adsorbents.

**Interactive behavior of metal ions**

The selectivity of adsorbents for Ni(II), Cd(II) and Cr(VI) in both binary and tertiary mixture was evaluated in terms of relative metal $i$ adsorption that is $R_i$ (%) which is defined as in Chang and Chen (1998). The percentage $R_i$ will determine whether the combinations in binary and tertiary system are antagonistic or synergistic in nature.

$$R_i = \frac{\text{metal } i \text{ adsorption capacity with coexistence of metal } j \text{ and } k}{\text{metal } i \text{ adsorption capacity without coexistence of metal } j \text{ and } k} \times 100$$

(4)

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**Table 4** Langmuir and Freundlich parameters for Ni(II), Cd(II) and Cr(VI) in mono, binary and tertiary system by SSC

| Metal combinations | SSC | | | | | |
|---|---|---|---|---|---|---|
| | Langmuir | | | Freundlich | | |
| | $Q_o$ | $b$ | $r^2$ | $K_f$ | $n$ | $r^2$ |
| Mono-component | | | | | | |
| Cr(VI) | 0.29 | 0.8 | 0.9873 | 1.8 | 3.6 | 0.8542 |
| Ni(II) | 0.24 | 1.5 | 0.9991 | 2.1 | 2.5 | 0.9123 |
| Cd(II) | 0.20 | 2.5 | 0.9986 | 0.9 | 1.8 | 0.9063 |
| Binary component | | | | | | |
| Ni(II) + Cd(II) | 0.12 | −158.7 | 0.9878 | 0.7 | 2.4 | 0.6737 |
| Ni(II) + Cr(VI) | 0.14 | −18.9 | 0.9916 | 0.12 | 3.4 | 0.9518 |
| Cd(II) + Ni(II) | 0.10 | −8.8 | 0.9824 | 0.1 | 2.1 | 0.9596 |
| Cd(II) + Cr(VI) | 0.09 | −6.3 | 0.9864 | 0.08 | 1.5 | 0.9785 |
| Cr(VI) + Ni(II) | 0.06 | −4.4 | 0.9817 | 0.06 | 1.1 | 0.9803 |
| Cr(VI) + Cd(II) | 0.05 | −3.2 | 0.9742 | 0.05 | 0.7 | 0.9798 |
| Tertiary component | | | | | | |
| Ni(II) + Cd(II) + Cr(VI) | 0.08 | −5.2 | 0.9843 | 0.07 | 1.3 | 0.9797 |
| Cd(II) + Ni(II) + Cr(VI) | 0.05 | −3.7 | 0.9785 | 0.06 | 0.9 | 0.9808 |
| Cr(VI) + Ni(II) + Cd(II) | 0.03 | −2.8 | 0.9685 | 0.3 | 0.5 | 0.1470 |

If $R_i > 100$ percent, it indicates that the interactive effect of a mixture of metals (say, $j$ and $k$) is synergistic, $R_i < 100$ % indicates antagonistic behavior and $R_i = 100$ % indicates non-interactive behavior. The values of $R_i$ were <100 % in all the binary and tertiary metal systems (Table 2). So, it was inferred that the interactions between different metal ions are antagonistic in nature. This may be due to the screening effect by the metals present in the solution (Sag and Kutsal 1996).

### Adsorption isotherms

The Langmuir and Freundlich adsorption isotherms were applied for mono, binary and tertiary systems. The value of correlation coefficient $r^2$ for Langmuir isotherm was found to be >0.95 for all the systems by both the adsorbents (Tables 3, 4). While the value of correlation coefficient $r^2$ for Freundlich isotherm varied for all the systems for both the adsorbents, it was very less for tertiary system (Tables 3, 4). The results clearly revealed that the adsorption capacity decreased from mono to binary and from binary to tertiary system due to the presence of other metal ions in the system. The maximum Langmuir capacity was found to be the highest for mono-component system, i.e., 0.26, 0.20 and 0.18 mg/g for Ni(II), Cd(II) and Cr(VI), respectively, by SHC and 0.29, 0.24 and 0.20 mg/g for Ni(II), Cd(II) and Cr(VI), respectively, by SSC, while it ranged between 0.15 and 0.02 mg/g for the binary system and between 0.05 and 0.02 mg/g for tertiary component system by SHC. The adsorption capacity ranged between 0.12 and 0.05 mg/g for the binary system and between 0.08

and 0.03 mg/g for tertiary component system by SSC (Tables 3, 4). The order of maximum adsorption capacity was found to be mono-component > binary component > tertiary component.

### Conclusion

Different parts of sunflower plant biomass were converted into two adsorbents. These adsorbents were employed for the adsorption of Ni(II), Cd(II) and Cr(VI) in mono, binary and multi-metal systems. The results showed the adsorption capacity of sunflower stem carbon was more than sunflower head carbon. It was also inferred from the data that adsorption capacity of the adsorbents decreased in the presence of co-cations. The adsorption capacity of both the adsorbents was lesser in multi-metal systems than binary and mono-metal systems, for any particular metal. This inhibitory effect of co-cations may be due to the competition and affinity of metal ions for different sites on the adsorbents. The value of $r^2$ was >0.95 for Langmuir isotherm in all the systems for both the adsorbents, thus showing the applicability of Langmuir model. The interactive effect was found to be antagonistic in both binary and tertiary systems indicated by values <100 in all the systems.

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## Nomenclature

| | |
|---|---|
| SHC | Sunflower head carbon |
| SSC | Sunflower stem carbon |
| BET | Brunauer–Emmett–Teller |
| SEM | Scanning electron microscope |
| EDX | Energy dispersive X-ray analysis |
| FT-IR | Fourier transform infrared microscopy |

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