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Chromium (VI) remediation in aqueous solution by waste products (peel and seed) of mango (*Mangifera indica* L.) cultivars

Caroline De Goes Sampaio[1,2] · Juliana Gaspar Alan E Silva[1] · Edy Sousa De Brito[3] · Helena Becker[4] ·
Maria Teresa Salles Trevisan[1] · Robert W. Owen[5,6]

Abstract

The surface group characteristics of mango cultivar peels and seeds were evaluated by infrared spectra, PZC, and functional group composition. The adsorption/reduction of chromium (VI) in aqueous solutions was investigated by varying pH, contact time, initial Cr(VI) concentration, and adsorbent amount. The results show that both peel and seed powders of the mango cultivars showed significant adsorption/reduction capacity for Cr(VI) and that the desorption process obeys pseudo-second-order kinetics. Optimal adsorption occurred at pH 1.0, using a Cr(VI) concentration of 100 mg/L. On average, at pH 1.0, and a concentration of 3 g/L, the maximum adsorption/reduction capacity of Cr(VI) was 83% (peels 76%, seeds 90%). Of the mango powders tested, the most efficient were Tommy seed (100%) and Coite peel (98%) followed by Coite seed (96%) and Tommy peel powders (95%). The adsorption/reduction of Cr(VI) was complete (100%) by the mango seed, in comparison to the peel powders (97%) after 180 min. The data indicates that mango waste products, such as seed and peel powders, are both excellent candidates for the remediation of Cr(VI) from aqueous systems and due to the higher concentration of gallates and galloyl glucosides, the mango seed powders should be the powders of choice for future remediation projects.

Keywords Adsorbent · Gallate glucosides · Mango powders · Peels · pH · Seeds

Abbreviations

MCP	Mango Coité peels
MCS	Mango Coité seeds
MMP	Mango Mallika peels
MMS	Mango Mallika seeds
MRP	Mango Rosa peels
MRS	Mango Rosa seeds
MTP	Mango Tommy peels
MTS	Mango Tommy seeds

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✉ Robert W. Owen
robert.owen@nct-heidelberg.de; r.owen@dkfz-heidelberg.de

Caroline De Goes Sampaio
carol-quimica@hotmail.com

Juliana Gaspar Alan E Silva
julianagaspar83@gmail.com

Edy Sousa De Brito
edy.brito@embrapa.br

Helena Becker
becker@ufc.br

Maria Teresa Salles Trevisan
mariattre@hotmail.com

[1] Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, CP 12200, Fortaleza, Ceará 60451-970, Brazil

[2] Instituto Federal de Educação, Ciência e Tecnologia do Ceará, Distrito Industrial I, Maracanaú, Ceará 61939-140, Brazil

[3] Embrapa Agroindústria Tropical, St. Dra Sara Mesquita, 2270, Pici, Fortaleza, Ceará 60511-110, Brazil

[4] Departamento de Química Analitica e Fisico-Quimica, Universidade Federal do Ceará, CP 12200, Fortaleza, Ceará 60451-970, Brazil

[5] Division of Preventive Oncology, National Center for Tumor Diseases, Im Neuenheimer Feld, 460 Heidelberg, Germany

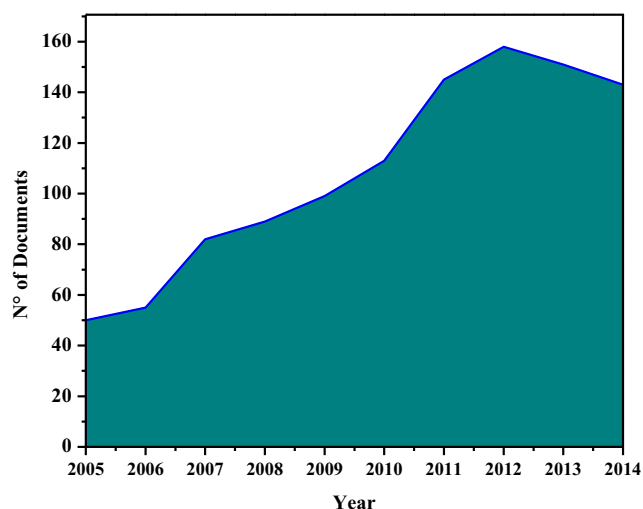[6] German Cancer Research Center (DKFZ), Im Neuenheimer Feld, 581 Heidelberg, Germany

Fig. 1 Search in Scopus for the term "chromium remediation" for papers published in the last 10 years. Search performed on April 24, 2015

Introduction

Chromium (VI) contamination in industrial waste waters has been an environmental problem for many years endangering both human and animal life Research into new materials that could be used efficiently in remediation is an important research topic nowadays (Dhal et al. 2013; Gerić et al. 2015). A search in Scopus for the term "chromium remediation" has shown a rapid growth in publications on this topic during the last decade (Fig. 1).

Studies show that by-products from agricultural materials can be used as low-cost adsorbents for chromium removal from aqueous media. Lignocellulosic residues (from agricultural waste) show adsorption ability as good as other natural adsorbents, but with some additional advantages such as very low or no production costs, high availability, and simple operational processes (Miretzky and Cirelli 2010).

Mango is a polyphenol-rich fruit from *Mangifera indica* L. Most of the polyphenols are present within its by-products (e.g., peels and seeds) and are discarded by the juice industry, because only the edible portion is used. Mango waste has been used as an environmental friendly biomaterial for different applications such as heavy metal removal, bioethanol, biohydrogen production, and others (Fernando et al. 2014; Iqbal et al. 2009; Mirabella et al. 2014; Redwood et al. 2012).

In this work, mango waste products were used in bioremediation studies with chromium (CrVI). This is the first study to evaluate mango waste as a potential sorbent material to remove CrVI from aqueous solutions.

Materials and methods

Chemicals

Folin-Ciocalteu reagent, methanol, 2,2-diphenyl-1-picrylhydrazyl radical (DPPH$^\bullet$), 2,2′-azino-bis(3-ethylbenzo-thiazoline-6-sulfonic acid diammonium salt) (ABTS), potassium persulfate, n-hexane, sodium nitrate (NaNO$_3$), sodium bicarbonate (NaHCO$_3$), methanol, HCl, sulfuric acid, sodium carbonate, sodium hydroxide, gallic acid (GA), and 1,5 diphenylcarbazide were supplied by Vetec Ltd (Rio de Janeiro, Brazil) and Trolox by Merck (St. Louis, MO, USA). All reagents were of analytical grade and stock solutions were prepared with ultrapure water.

Seeds and peels of Mango cultivars

Four mango cultivars grown in the State of Ceará, in the northeast of Brazil, were used in this study. The cultivars studied were Coité, Mallika, Rosa, and Tommy. All were obtained from EMBRAPA—Agroindústria Tropical (CNPAT) (Fortaleza, CE, Brazil). Peels and whole seeds were manually separated from the fruit, washed with distilled water, oven-dried at 50 °C (48 h), triturated, and sifted through 0.7-mm (25 mesh) standard sieves. The materials were stored at room temperature. Eight different materials were used in this study: mango Coité peels (MCP), mango Coité seeds (MCS), mango Mallika peels (MMP), mango Mallika seeds (MMS), mango Rosa peels (MRP), mango Rosa seeds (MRS), mango Tommy peels (MTP), and mango Tommy seeds (MTS).

Table 1 Yield of solvent extracts of the mango peel and seed powders of the four cultivars

Mango cultivars	Dry weight extracted (g)	Hexane extract yield (%)	Methanol extract yield (%)
MCP	3.1433	1.34	43.80
MCS	3.1416	2.37	3.72
MMP	3.2077	1.60	35.30
MMS	3.2476	0.85	4.00
MRP	3.3478	1.58	38.22
MRS	3.2738	0.94	2.20
MTP	3.0625	0.96	54.82
MTS	3.3490	3.67	14.96

Table 2 Surface functional groups of Coité, Mallika, Rosa, and Tommy cultivar peels

Surface groups	Mango cultivar peels ($\mu M/g$) $\pm$ SD			
	Coité	Mallika	Rosa	Tommy
Carboxylic	81.85 ± 7.31	96.32 ± 7.80	259.11 ± 23.01	163.78 ± 5.09
Lactone	42.76 ± 2.06	57.56 ± 6.41	5.02 ± 0.15	50.33 ± 1.61
Phenol	301.66 ± 5.43	530.83 ± 16.73	45.62 ± 0.87	544.41 ± 2.49
Carbonyl	3732.67 ± 18.51	5796.43 ± 60.43	585.13 ± 9.03	7310.97 ± 29.90
Basic	–	–	–	–

Preparation of mango waste extracts

Raw extracts of the powders (Table 1) prepared from the peels and seeds of the fruits were obtained by Soxhlet extraction. Initially, the powders were extracted with *n*-hexane for 3 h, allowed to dry, and further extracted (3×3 h) with methanol. Methanol extracts were pooled, and the solvent was removed by rotary evaporation. The residues were dried to constant weight (Table 1) and stored at 27 °C wrapped in aluminum foil to avoid exposure to light.

Chemical characterization of the surface compounds on peels and seeds of mango cultivars

Fourier transform IR spectra (FTIR) for all the materials were recorded with a Shimadzu IR spectrophotometer (model 8300) in the range of 400 to 4000 cm^{-1} as KBr pellets. Acid and basic functional groups on the surface of the seeds and peels were determined by the Boehm titration method (Valdés et al. 2002; Oliveira et al. 2008). Solutions of NaHCO$_3$ (0.1 mM), Na$_2$CO$_3$ (0.05 mM), NaOH (0.02 and 0.1 mM), and HC1 (0.02 mM) were prepared using deionized water. A volume of 20 mL of these solutions was added to Erhlenmeyer flasks (100 mL) containing 200 mg of each mango by-product for all cultivars. The samples were shaken at 120 rpm and five blanks were used. After 24 h, the solid and aqueous phases were separated by decantation and filtration. Excess of base or acid was determined by back titration, using hydrochloric acid (0.02 and 0.1 mM) and sodium hydroxide (0.02 mM) solutions. The point of zero charge (PZC) of mango cultivars was determined by a batch equilibration technique (Valdes et al

2002) in NaNO$_3$ solution. The pH of each solution was measured using a digital pH meter. PZC was determined as the converging pH value from the pH versus biosorbent mass curve.

Determination of total phenolic content in the peels and seeds of Mango cultivars

Total phenolic content was determined using the Folin-Ciocalteu spectrophotometric assay (Bonoli et al. 2004).

Antioxidant capacity

DPPH assay

Evaluation of the antioxidant capacity by the DPPH assay was performed according to Brand-Williams et al. (1995) with the modifications of Alves et al. (2008).

ABTS assay

Evaluation of the antioxidant capacity by the ABTS assay was performed according to Re et al. (1999).

Analytical HPLC-ESI-MS

Analytical HPLC-ESI-MS analyses were conducted as described by Barreto et al. (2008) except that a C18 Phenomenex Gemini column (Aschaffenburg, Germany) was used.

Table 3 Surface functional groups of Coité, Mallika, Rosa, and Tommy cultivar seeds

Surface groups	Mango cultivar seeds ($\mu M/g$) $\pm$ SD			
	Coité	Mallika	Rosa	Tommy
Carboxylic	16.19 ± 2.51	39.39 ± 2.67	13.04 ± 0.70	89.97 ± 5.23
Lactone	12.61 ± 0.28	17.14 ± 2.52	111.72 ± 0.72	44.47 ± 3.28
Phenol	290.59 ± 1.53	435.92 ± 6.49	526.54 ± 7.23	567.74 ± 12.01
Carbonyl	3023.74 ± 26.9	4405.05 ± 19.68	8779.39 ± 10.47	6277.74 ± 200.27
Basic	94.13 ± 9.50	96.92 ± 8.00	235.01 ± 10.67	25.07 ± 0.13

Table 4 Assignment of bands in FTIR of the mango peel and seed powders of the four cultivars (Poonkuzhali et al. 2014; Netzahuatl-Munõz et al. 2012)

Mango cultivars (FTIR, cm^{-1})								FTIR assignment
MCP	MCS	MMP	MMS	MRP	MRS	MTP	MTS	
1745	–	1738	–	1749	–	1749	1719	ν C=O of carboxylic acids and ester
1624	1643	1640	1645	1643	1638	1633	1638	ν C=O of carbonyl groups
–	–	–	–	–	–	–	1525	C=C aromatic ring stretching
1448	1459	–	–	–	1444	–	1453	Methylene C–H bending
–	–	1370	1377	–	1372	–	1359	Methyl C–H bending
1232	–	1240	–	1242	–	1247	–	C–O stretch of carboxylic acids
–	1153	–	1150	–	1153	–	1161	ν C–O–C of ester
–	–	–	1082	–	–	–	1080	ν C–O–C of ester
1058	1039	1049	1020	1057	1040	1025	1024	Vibration involving ν C–O

Batch equilibrium experiments

Batch equilibrium experiments with MCP, MCR, MMP, MMR, MRP, MRS, MTP, MTS were performed in 250-mL Erlenmeyer flasks, by using magnetic stirrers with a fixed setting to achieve a constant speed (120 rpm) at ambient temperature (25 ± 2 °C). A stock solution of 1000 mg/L Cr(VI) was prepared by dissolving 2.8341 g $K_2Cr_2O_7$ in 1000 mL of ultrapure water. Required concentrations of Cr(VI) standards were prepared by appropriate dilution of the above Cr(VI) stock solution. In the first set of experiments, H_2SO_4 or NaOH 1 M was used for regulating the pH range. The percentage removal of Cr(VI) was studied at various pH values (1, 2, 3, 5, 12), adsorbent dose (1, 2, 3, and 4 g/L), contact time (5, 20, 30, 60, 90, 120, and 180 min), and initial Cr(VI) concentration (50, 100, 150, 200, and 300 mg/L). The hexavalent chromium concentration was estimated according to APHA (2005) by a colorimetric method with 1,5-diphenylcarbazide. Total chromium concentration was determined by atomic absorption spectrometry (AAS) after the adsorption test. The reduced Cr(III) was calculated by the difference between total Cr and Cr(VI) in solution. The percentage removal of Cr(VI) was calculated using Eq. (1):

$$R(\%) = (C_o - C_e / C_o) \times 100 \qquad (1)$$

where C_o (mg/L) is the initial concentration and C_e (mg/L) is the equilibrium metal concentration. The adsorption capacity, q (mg/g), is defined as the mass of substrate bound by a gram of adsorbent. Equation (2) below shows the mathematical equation for the calculation, of the adsorption capacity, in which C_o and C_e are as described for Eq. (1), V(L) is the volume of the sample solution, and W(g) is the mass of the adsorbent:

$$q(mg/g) = ((C_o - C_e)) \times V/m \qquad (2)$$

Result and discussion

### Surface characteristics of mango seeds and peels from four cultivars

When studying possible materials as adsorbents, it is necessary to make a preliminary assessment of the characteristics of the surface groups. This is important to evaluate the major groups that may contribute to the adsorption or reduction process, regardless of what mechanisms are involved (Zhang et al. 2010). The surface groups of mango peels and seeds may have acid (carboxylic acids, carboxy lactone, carbonyl, and phenolic) and basic (pyrone and chromen) properties (Wei et al. 2013; Guilarduci et al. 2006). In this study MCP, MCS, MMP, MMS, MRP, MRS, MTP, and MTS were initially characterized using the Boehm titration method, by FTIR and determination of PZC. The indirect quantitation of these groups on the surface of peels and seeds are described in Tables 2 and 3, respectively.

As shown in Table 2, it was observed that all mango peels have a greater amount of surface carboxylic groups compared to the seeds (Table 3). Of these, MRP and MTP powders contained a greater number of surface carboxylic groups (259.11 and 163.78 μM, respectively). When analyzing the main assignment of bands from the IR spectra (Table 4),

Table 5 PZC of the mango peel and seed powders of the four cultivars

Mango cultivars		PZC
Coite	Peels	3.05
	Seeds	5.90
Mallika	Peels	3.30
	Seeds	5.40
Rosa	Peels	3.30
	Seeds	6.70
Tommy	Peels	3.00
	Seeds	3.80

Fig. 2 Analytical reverse-phase of HPLC chromatogram of a methanol extract of mango Tommy seeds. Peak 1 gallic acid; peak 2 3,4-dihydroxybenzoic acid, peak 3 methyl gallate, peak 4 mangiferin, peak 5 pentagallate, peak 6 ellagic acid, peak 7 hexagallate, peak 8 heptagallate, peak 9 octagallate
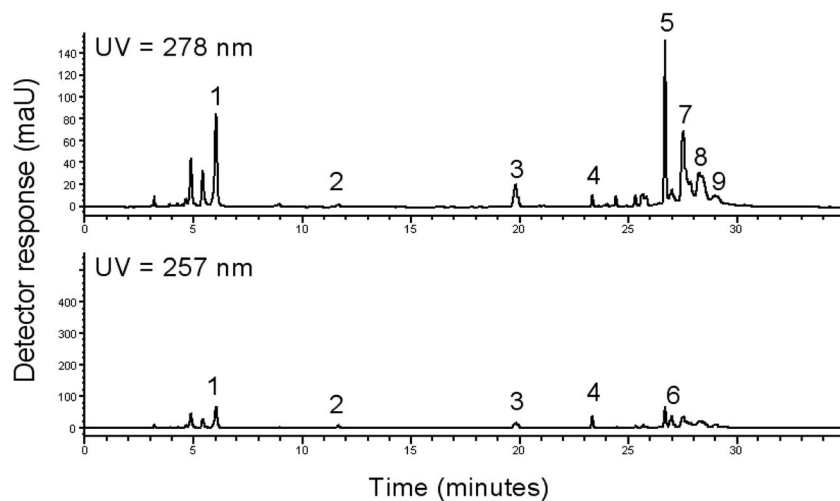
signals of carboxylic acids were observed in mango peels of all cultivars, confirming the data obtained from the surface group Boehm titration method. The regions between 1750 and 1600 cm^{-1} are characteristic of carbonyl groups. An intense band at 1749 cm^{-1} in the peels of mango cultivars is indicative of a C=O group from carboxylic acids or their esters (Netzahuatl-Munõz et al. 2012). The axial deformation vibration of a C–O bond, which appears in the region 1240 cm^{-1}, may suggest the presence of both carboxylic acids such as esters or lactones attached to aromatic groups (Sampaio et al. 2015a, b; Kaya et al. 2014).

The comparison of the IR spectra and surface functional groups gave some valuable information about the presence of adsorbent groups in mango cultivars, which supports the relation between chromium sequestration/reduction and the concentration of mango peels and seeds used.

The MTS cultivar had the highest amount of surface phenolic groups (567.74 μM) and showed a band in the IR spectra

at 1525 cm^{-1} characteristic of C=C stretching of phenolics. Phenolic and carbonyl groups are responsible for much of the removal of heavy metals, and these being the predominant groups in good adsorbents (Pagnanelli et al. 2003). Therefore, MTS is an important cultivar of mango that has a superior capacity to remove or reduce Cr(VI) from aqueous solutions. The presence of these groups provides a more hydrophilic character to the adsorbent, facilitating their interaction with adsorbate (in this study, dissolved chromium). The compounds present on the surface of adsorbents are associated with large amounts of oxygen (carbonilic groups) and have anion exchange properties.

As reported by Mimura et al. (2010), the point of zero charge (PZC) and the pH (Jung et al. 2013) are also important factors relevant to the surfaces of adsorbent materials.

In this study, the mean PZC values of the peels and seeds of the four mango cultivars determined from the titration curves were 3.16 and 5.45, respectively (Table 5). In general,

Table 6 Individual polyphenolic compounds identified by HPLC-DAD-ESI-MS in methanol extracts of the mango peel and seed powders of the four cultivars

Phenolic compounds	DAD, λmax (nm)	HPLC-ESI-MS (m/z)		
		[M–H]$^-$	[2 M–H]$^-$	[M–2H]$^-$/2
Gallic acid	226, 278	169.1	339.1	
3,4-Dihydroxy benzoic acid	225, 289	153.1	307.1	
Methyl gallate	226, 272	183.1	367.1	
Brevifolin carboxylic acid	226, 276, 350	291.1	583.1	
Methyl brevifolin carboxylate	265, 364	305.1	611.0	
Mangiferin	240, 258, 276, 320, 368	421.1	843.1	
Isomangiferin	257, 320, 368	421.1		
Ellagic acid	257, 308, 367	301.1	603.1	
Tetra-*O*-galloyl-glucoside	226, 278	787.0		393.1
Penta-*O*-galloyl-glucoside	225, 280	939.1		469.2
Hexa-*O*-galloyl-glucoside	226, 280	1091.1		545.2
Hepta-*O*-galloyl-glucoside	225, 278	1243.1		621.2
Octa-*O*-galloyl-glucoside	225, 280	1395.1		697.2

Table 7 Content (g/kg dry material) of individual polyphenolic compounds in methanol extracts of the mango peel and seed powders of the four cultivars

Phenolic compounds	g/kg of extract							
	MMP	MMS	MCP	MCS	MRP	MRS	MTP	MTS
Gallic acid	1.22	13.75	1.70	3.65	1.02	2.81	2.81	18.96
3,4-Dihydroxy benzoic acid	2.13	–	–	–	5.86	–	0.13	1.60
Methyl gallate	–	10.42	–	21.92	–	9.83	1.54	6.47
Brevifolin carboxylic acid	–	1.36	–	5.07	–	0.22	–	–
Methyl brevifolin carboxylate	–	–	–	6.30	–	–	–	–
Mangiferin	11.23	52.95	–	19.35	15.36	3.03	2.42	8.82
Homomangiferin	–	–	–	–	0.79	–	0.31	–
Ellagic acid	0.53	18.53	2.32	13.73	2.74	11.36	0.74	3.72
Tetra-O-galloyl-glucoside	–	6.02	–	9.27	–	–	–	–
Penta-O-galloyl-glucoside	0.29	12.95	1.89	29.45	–	4.05	0.63	22.61
Hexa-O-galloyl-glucoside	–	–	–	–	–	–	–	24.57
Hepta-O-galloyl-glucoside	–	–	–	–	–	–	–	26.72
Octa-O-galloyl-glucoside	–	–	–	–	–	–	–	10.48
Total (g/kg)	15.40	115.98	5.91	108.74	25.77	31.30	8.58	123.95

biomaterials which have a high content of acid groups have low PZC values (Aygün et al. 2003).

At a pH below the PZC, the surfaces of peels and seeds of mango cultivars are positively charged and thus effective in removing negatively charged species ($HCrO_4^-$), which is the prevalent species of Cr(VI) at acid pH in aqueous solution, while at pH values above the PZC, the composite surface is negatively charged.

Identification of phenolic compounds in mango peels and seeds from the four cultivars by HPLC-DAD-ESI-MS

HPLC-DAD-ESI-MS in negative-ion mode was used to analyze and identify the phenolic compounds present in methanol extracts of mango peels and seeds from the four cultivars,

which may be responsible for removal or reduction of Cr(VI) in aqueous solutions. An analytical HPLC chromatogram of the methanol seed extract of the cultivar Tommy is shown in Fig. 2 as a general example.

The structures of the compounds were identified in peels and seeds by their pseudomolecular ions [M–H]⁻, and fragmentation patterns in the mass spectrometer, along with their characteristic UV spectra (Table 6). The structures were confirmed by comparison with literature data (Barreto et al. 2008; Ribeiro et al. 2008).

The quantity (Table 6) of the phenolic compounds in grams per kilogram in the extracts was calculated from calibration curves of the purified compounds. Gallic acid, mangiferin, ellagic acid, and penta-O-galloyl-glucoside were the predominant compounds in all samples. These compounds (Table 7) may be partly responsible for both adsorption and reduction of

Table 8 Quantitation of total polyphenolic compounds and antioxidant capacity in methanol extracts of the mango peel and seed powders of the four mango cultivars
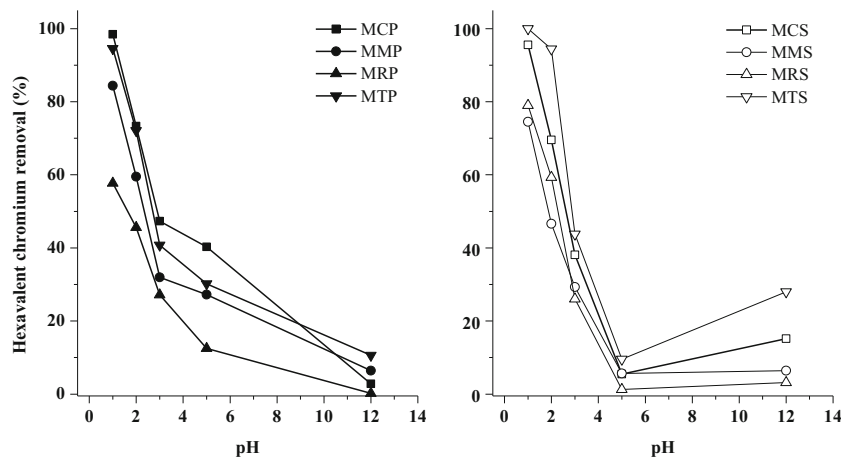
Mango Cultivars	Antioxidant capacity (μM TE[*]/g extracts ± SD)		Total phenolics (mg GAE[**]/g extracts ± DP)
	DPPH	ABTS-TEAC[***]	
MCP	631.89 ± 33.73	1484.89 ± 134.26	95.10 ± 3.78
MCS	1029.22 ± 10.15	1736.22 ± 92.99	180.61 ± 15.69
MMP	478.11 ± 22.31	1057.56 ± 37.72	64.90 ± 0.53
MMS	1098.56 ± 73.12	1834.67 ± 25.96	186.57 ± 7.44
MRP	439.95 ± 17.23	1217.78 ± 24.46	64.14 ± 2.75
MRS	521.78 ± 25.60	460.44 ± 38.50	78.18 ± 1.05
MTP	402.06 ± 12.77	1026.67 ± 26.56	29.34 ± 1.31
MTS	1606.28 ± 14.80	3093.33 ± 108.94	240.76 ± 24.15

[*] *TE* Trolox equivalent

[**] *GAE* gallic acid equivalents

[***] *TEAC*:Trolox equivalent antioxidant capacity (μM Trolox equivalents/g dry extract)

Cr(VI) to Cr(III) (Gong et al. 2013; Ferreira et al. 2013), because materials rich in polyphenolic compounds exhibit high affinity for heavy metal ions (Chand et al. 2009).

Antioxidant capacity

The methanol extracts of each mango cultivar were evaluated in the DPPH and ABTS, in vitro assays for their antioxidant capacities, and the results are shown in Table 8. The application of materials with antioxidant capacity, or the use of chelating agents, can increase the ability to sequester metals (Soudek et al. 2014).

In this respect, the antioxidant assays of the mango cultivar extracts showed a fairly broad range of activity. The extracts of Tommy seeds (1606 and 3093 μM TE/g) were the most effective in the DPPH and ABTS assays, respectively, containing the highest amount of total phenolic compounds as ascertained in the Folin-Ciocalteau (241 g GAE/kg) and HPLC-based (124 g/kg) assays. These results may be related to the high concentration of gallic acid, methyl gallate, and galloyl glucosides in this extract (Barreto et al. 2008) which can also be associated with synergism between bioactive compounds present in this species (Kim et al. 2010). In support of

this, the correlation between the concentrations of total gallates in the mango seed powders and adsorption of Cr(VI) was very strong ($r = 0.95$, $p = 0.055$).

Gallic acid, methyl gallate, and penta-*O*-galloyl-glucoside showed excellent antioxidant capacity in the DPPH and ORAC assays, compared to the reference standards Trolox and ascorbic acid (Barreto et al. 2008), confirming the current data. This indicates that these compounds may be responsible for the sequestration and reduction of Cr(VI) to CR (III). Poonkuzhali et al. (2014) also inferred that the phenolic compounds, ferulic acid, kaempferol, and β-carboline, ostensibly present in extracts of *Aerva lanata* L., were responsible for the reduction of hexavalent chromium. On close inspection however, Poonkuzhali et al. (2014), despite their claims, provide no evidence whatsoever that the extracts of this plant contain these phenolic compounds. The LC-MS data presented is totally erroneous.

Effect of initial solution pH

In order to obtain a better adsorption effect, it is necessary to vary different experimental conditions to obtain optimal
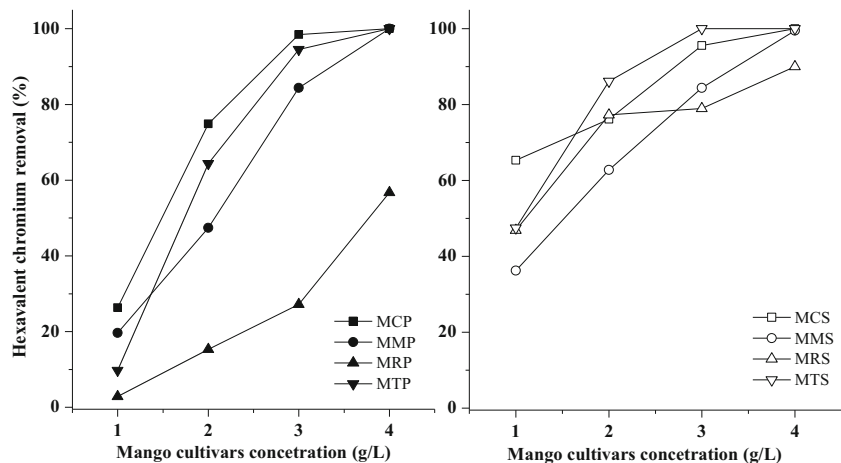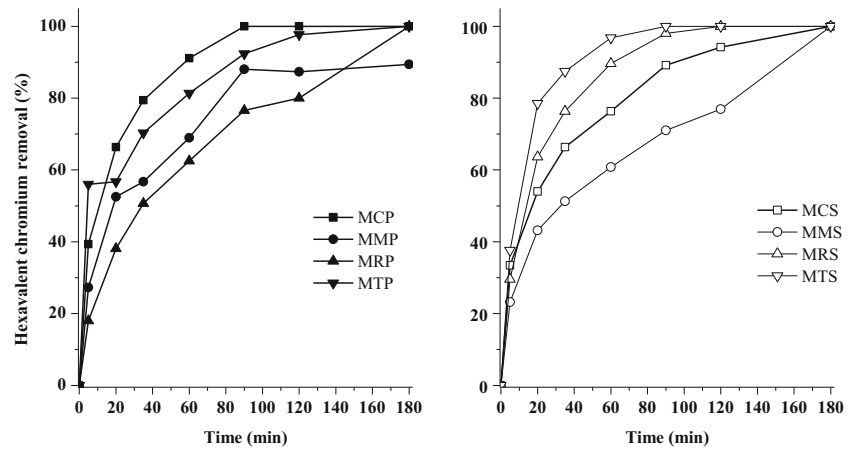
Fig. 5 Effect of contact time on the removal of Cr(VI) by the peels and seeds of mango cultivars [MCP(■), MMP (●), MRP (▲), MTP (▼), MCS (□), MMS (○), MRS (△), MTS (▽)]. Conditions: [Cr(VI)] = 100 mg/L, particle size 25 mesh, 120 rpm and room temperature (25 ± 1 °C)

parameters. pH is the single most important parameter for metal adsorption (Zhang et al. 2010) because it affects the surface charge of the adsorbent material (Netzahuatl-Munõz et al. 2012) and the degree of ionization and specification of adsorbate.

The removal of Cr(VI) was studied as a function of pH over a pH range between 1.0 and 12 with MCP, MCS, MMP, MMS, MRP, MRS, MTP, and MTS ([Cr(VI)]—100 mg/L and 3 g/L of adsorbent) as shown in Fig. 3. A high selectivity for Cr(VI) removal at pH < 4 was observed for all mango cultivars.

The efficiency of Cr(VI) removal was much higher at low pH values. A sharp decrease in Cr(VI) ion removal occurred, when the pH value of the solutions increased from 1.0 to 12.0. The maximum removal of Cr(VI) ions was obtained at pH 1.0. The main explanation for the large influence of solution pH may be due to the variety of hexavalent chromium (H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$) ions present. However, it was observed previously (Kaya et al. 2014; Khosravi et al. 2014; Dittert et al. 2014; Sampaio et al. 2015a, b) that at pH 1.0, the predominant species of chromium is $HCrO_4^-$. Similar qualitative observations were reported for the removal of Cr(VI) by grape waste (Chand et al. 2009), *Cupressus lusitanica* bark (Netzahuatl-Munõz et al. 2012), fungal biomass of *Phanerochaete chrysosporium* (Marandi 2011), and *Ocimum americanum* L. seed (Levankumar et al. 2009).

In our study, the PZC values vary from 3.16–5.45 for the mango cultivars. This is in agreement with our experimental observations, showing very low removal at pH > 4 whereas at pH 1.0, the –OH group is protonated and thereby facilitates the binding of $HCrO_4^-$ ions to the surface of the adsorbent, which results in higher removal of the metal. Park et al. (2007) also demonstrated that the reaction rate constant is strongly pH dependent.

Fig. 6 Effect of variation of initial concentration of Cr(VI) on the removal of Cr(VI) by (**a**) MCP, (**b**) MCS, (**c**) MMP, (**d**) MMS, (**e**) MRP, (**f**) MRS, (**g**) MTP, and (**h**) MTS
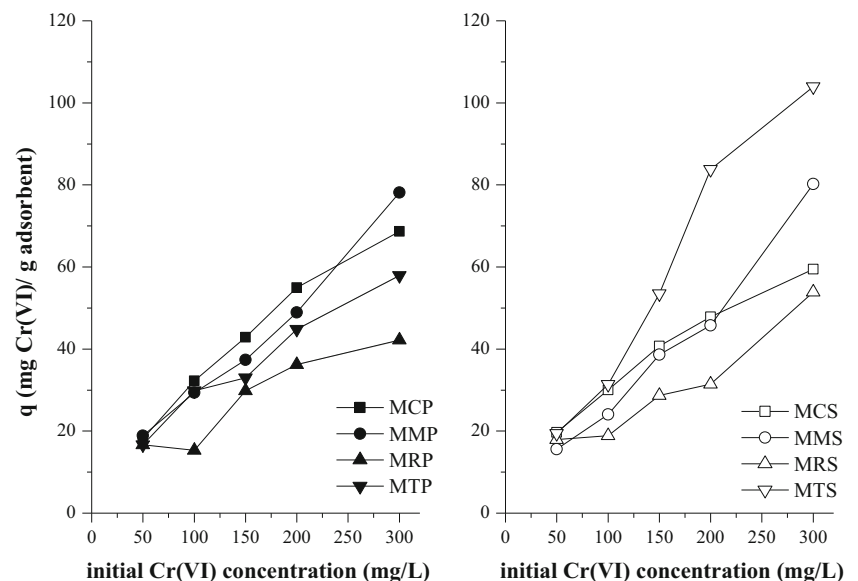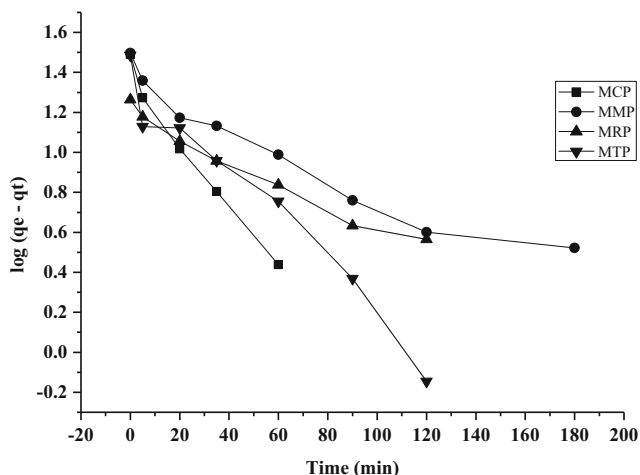
Fig. 7 Kinetic model of pseudo-first-order adsorption of Cr(VI) by the peels of mango cultivars Coité, Mallika, Rosa, and Tommy. Conditions: [Cr(VI)] = 100 mg/L, pH 1.0, particle size 25 mesh, 120 rpm and room temperature (25 ± 1 °C)

Fig. 9 Kinetic model of pseudo-second-order adsorption of Cr(VI) by the peels of mango cultivars Coité, Mallika, Rosa, and Tommy. Conditions: [Cr(VI)] = 100 mg/L, pH 1.0, particle size 25 mesh, 120 rpm and room temperature (25 ± 1 °C)

Effect of adsorbent dose

To determine the minimum amount of adsorbent required for removing Cr(VI), an experiment was conducted with concentrations of adsorbent ranging from 1 to 4 g/L at a Cr(VI) concentration of 100 mg/L and pH 1.

The results (Fig. 4) show that increasing the adsorbent mass influenced the removal of Cr(VI). The maximal removal (100%) was affected by 4 g/L of the Coite, Mallika, and Tommy powders. But for the Rosa cultivar (peel and seed), an increase to 5 g/L was required for 100% removal.

This indicates that the cultivar Rosa has a chromium removal capacity, lower than the other mango varieties studied. In support of this, correlations with the total and individual content of phenolic compounds in the Rosa powder extracts,
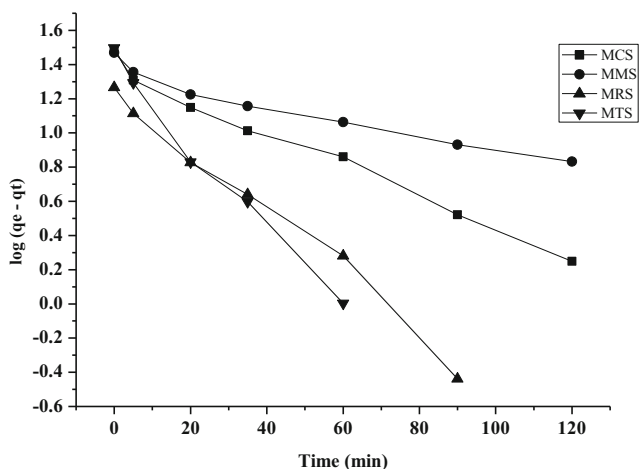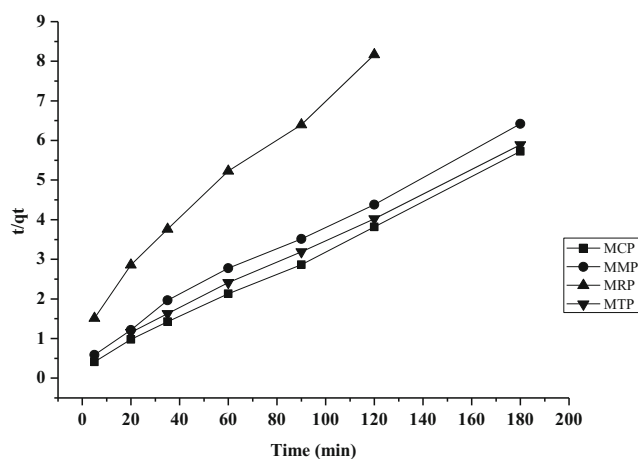
or on the surface of the matrix, deemed mainly responsible for the removal of metals in an aqueous medium (Suksabye et al. 2007), were not evident.

Our data is in stark contrast to that of Nadeem et al. (2015) who showed a dramatic decrease in the sequestration of Cu^{2+} and Zn^{2+} with increasing dose of mango biomass in the range 1–5 g/L.

Effect of contact time and initial Cr(VI) concentration

The results of the adsorption studies are shown in Fig. 5. As can be seen, the removal capacity of the powders, varied among the cultivars. In the case of MCP and MTS, complete removal occurred after 90 min, for MRS after 120 min, and for MRP, MTP, MCS, and MMS after 180 min, whereas 100% removal was not affected by MMP (90% at 180 min).
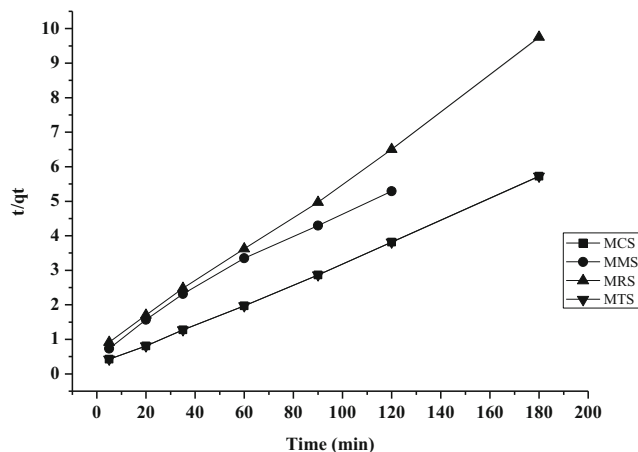

Fig. 8 Kinetic model of pseudo-first-order adsorption of Cr(VI) by the seeds of mango cultivars Coité, Mallika, Rosa, and Tommy. Conditions: [Cr(VI)] = 100 mg/L, pH 1.0, particle size 25 mesh, 120 rpm and room temperature (25 ± 1 °C)

Fig. 10 Kinetic model of pseudo-second-order adsorption of Cr(VI) by the seeds of mango cultivars Coité, Mallika, Rosa, and Tommy. Conditions: [Cr(VI)] = 100 mg/L, pH 1.0, particle size 25 mesh, 120 rpm and room temperature (25 ± 1 °C)

All adsorbents removed approximately 40% of Cr(VI) from aqueous solution during the first 20 min. Deveci and Kar (2013) argue that this rapid sequestration is due to the strong attraction between the metal ions and the active sites on the surface of the adsorbent. Furthermore, Kumar et al. (2008) state that, thereafter, removal of Cr(VI) occurs more slowly, due to a reduction in available sites on the surface of the adsorbent, compared with the initial stage. The results demonstrate that a 180-min contact time is sufficient for 100% removal of Cr(VI) by 87.5% of the adsorbents under optimal conditions in this study.

The data generated is similar to that described by Marandi (2011), who studied Cr(VI) removal capacity, using biomass from *Phanerochaete chrysosporium* with maximal removal after 2 h. In contrast, Dittert et al. (2014) reported a time span of 8 h for maximal removal of Cr(VI) from aqueous solutions by *Laminaria digitata* micro-algae biomass.

Experiments comparing the differential capacity of mango peel and seed powders, to adsorb initial concentrations of Cr(VI), were conducted in the range 50–300 mg/L. The data shows (Fig. 6) that in adsorption capacity terms (mg Cr(VI)/g adsorbent), on average at 50 mg/L chromium ions, peel powders (17.57 ± 1.10) and seed powders (18.16 ± 1.88) were very similar after 180 min of contact time. At 300 mg/L chromium ions, the adsorption capacity (q) values of both peel and seed powders were 61.72 ± 15.43 and 74.38 ± 22.73, respectively. Of interest is that at 50 mg/L, the peel powders gave values close to the seed powders, whereas at 300 mg/L, a larger difference was observed in the average adsorption capacity between the peels and seeds, with the seeds adsorbing approximately 13 mg more. The most effective powder was MTS with an adsorption capacity of 103.94 mg/g, when the concentration of the metal was 300 mg/L. These data are in good agreement with that of Nadeem et al. (2015) for the sequestration of Cu^{2+} and Zn^{2+} ions by mango biomass.

Fig. 11 Total chromium, Cr(VI), and Cr(III) in aqueous solution following treatment with peels and seeds of mango cultivars: **a** MCP, **b** MCS, **c** MMP, **d** MMS, **e** MRP, **f** MRS, **g** MTP, and **h** MTS

Adsorption kinetics

As reported by Lagergren (1898), Ho and Mckay (1998), and Ho et al. (2000) kinetic studies are important for determining the adsorption rate, and solute gain rate, which affects the endurance time in the adsorption process and defines the time relevant to the efficiency of an adsorbent. In this study, two models, which addressed pseudo-first-order and pseudo-second-order kinetics, were tested to predict the adsorption data of Cr(VI) ions as a function of time. The data for the pseudo-first-order and pseudo-second-order kinetic models is shown in Figs. 7–8 and 9–10, respectively.

Our results show that the experimental values (q) are in good agreement with the calculated values for the pseudo-second-order model (Table 9). The behavior of pseudo-second-order kinetics for the experimental data indicates that the main type of control mechanism is the chemical adsorption interaction, while second-order kinetics is related to Cr(VI) removal by various adsorbents (Deveci and Kar 2013, Panda et al. 2011).
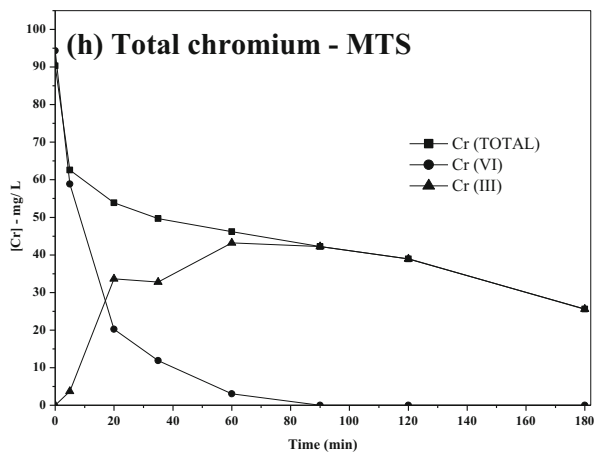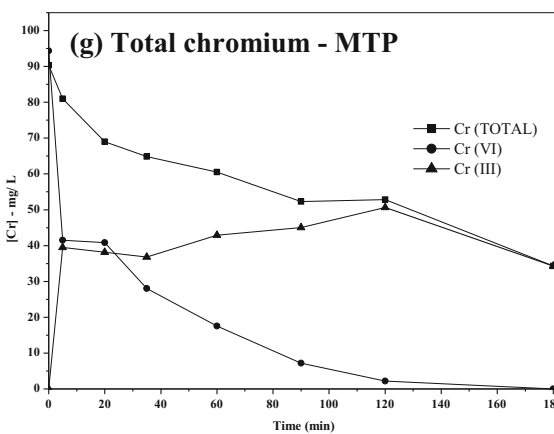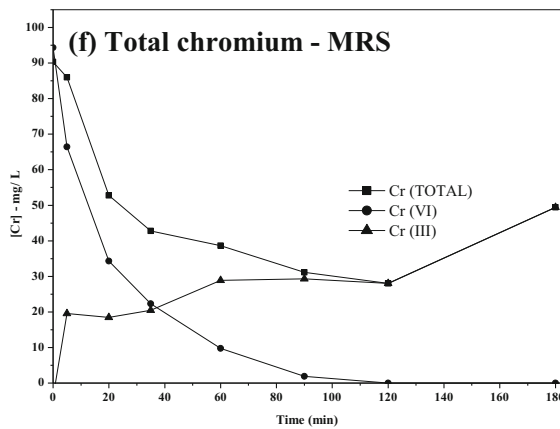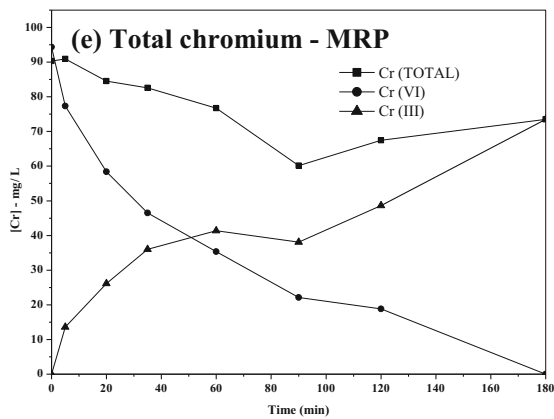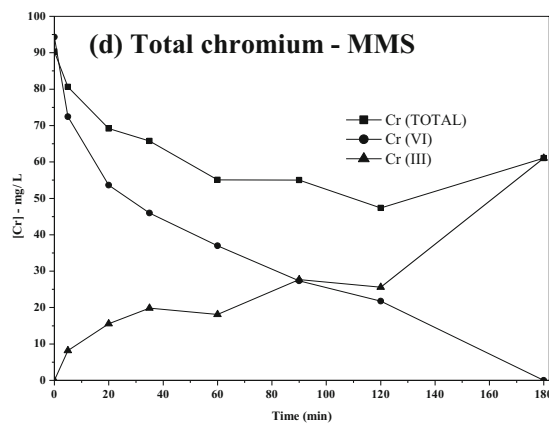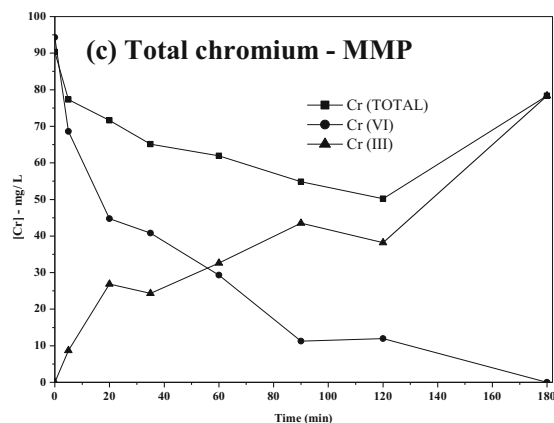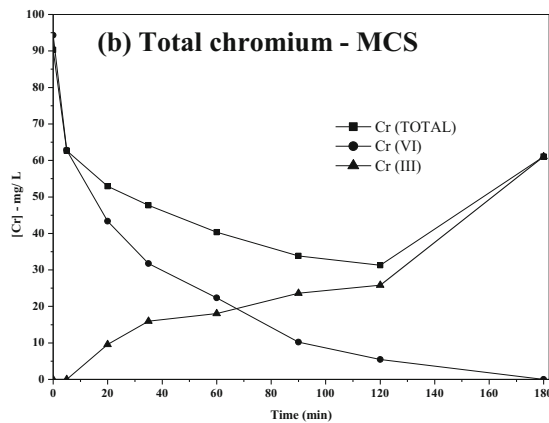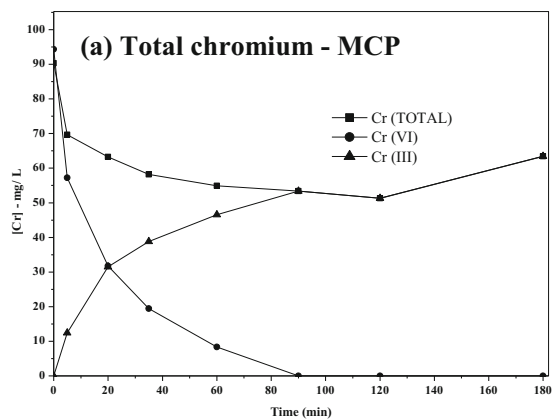
Reduction and adsorption of chromium

Cr(VI) removal is also based on a mechanism that includes reduction of Cr(VI) to Cr(III), via the oxidation of biomass in acidic solution, and further chemical binding of Cr(III) to negatively charged carbonyl groups (Dittert et al. 2014). In order to elucidate the reduction of Cr(VI), after interaction with peel and seed mango biomass from the four cultivars, both Cr(VI) and Cr(III) concentrations in solution were measured at pH 1; [Cr(VI)] = 100 mg/L; 3 g biomass/L; 25 mesh and 120 rpm as shown in Fig. 11.

Conversion of Cr(VI) to Cr(III) ranged from 40–80% (Fig. 11), indicating the reductive power of the mango waste material.

Table 9 Adsorption kinetic parameters of peel and seed powders of mango cultivars

Mango cultivar	C_o (mg/L)	$q_{e\ (EXP)}$	Pseudo-first order			Pseudo-second order		
			$q_{c\ (CAL)}$	K_1 (g/mg/min)	R^2	$q_{c\ (CAL)}$	K_2 (g/mg/min)	R^2
MCP	94.32	30.92	25.33	0.038	0.97	31.78	0.0028	1.00
MCS	94.32	30.60	24.77	0.022	0.98	31.78	0.0028	1.00
MMP	94.32	28.05	25.84	0.028	0.97	31.06	0.0016	0.99
MMS	94.32	29.49	23.85	0.011	0.94	29.71	0.0019	0.99
MRP	94.32	18.36	15.83	0.013	0.97	18.12	0.0552	0.99
MRS	94.32	18.46	17.40	0.041	0.98	18.19	0.0507	1.00
MTP	94.32	30.56	17.40	0.041	0.98	34.25	0.0291	1.00
MTS	94.32	31.44	26.45	0.056	0.98	33.00	0.0303	1.00

(a) Total chromium - MCP

(b) Total chromium - MCS

(c) Total chromium - MMP

(d) Total chromium - MMS

(e) Total chromium - MRP

(f) Total chromium - MRS

(g) Total chromium - MTP

(h) Total chromium - MTS

The adsorption of Cr(VI), plus conversion to non-toxic CR(III), was complete after 3 h by all powders, indicating the dual chromium remediation modes of mango waste products.

Conclusions

The optimal removal of Cr(VI) from model aqueous solutions, by the mango cultivar powders, occurred at pH 1.0, as determined at a sorbent concentration of 3 g/L, and a contact time of 180 min. The data indicates that low-cost waste products of mango juice production (seed and peel powders) may have utility in remediation of toxic Cr(VI) species from aquatic systems, thereby decreasing the risk to human and animal health.

Compliance with ethical standards

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

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