# Removal of Cr(VI) from synthetic wastewater by adsorption onto coffee ground and mixed waste tea

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## HIGHLIGHTS

- Recycle of mixed waste tea and coffee ground as alternative adsorbents for Cr(VI) removal.
- Both adsorbents completely removed 30 mg $L^{-1}$ Cr(VI) within 180 min and could be reused for four times.
- Carbon and oxygen functional groups on the surface of both adsorbents involved in Cr(VI) adsorption.
- Kinetic study matched well with the Freundlich and pseudo-second-order model for the 10-250 mg $L^{-1}$ concentration range.
- A 100 L of reactor containing mixed waste tea showed the breakthrough time of adsorption as 30 min in 100 mg $L^{-1}$ Cr(VI).

## ARTICLE INFO

## ABSTRACT

We attempted to recycle mixed waste tea and coffee ground as alternative low-cost adsorbents for Cr(VI) removal. The adsorption parameters optimized were: initial Cr(VI) concentration (10–30 mg $L^{-1}$), contact time (180 min), adsorbent dose (2.0 g $L^{-1}$), initial pH (2.0), temperature (30–50 °C), and agitation speed (250 rpm). Freundlich isotherm was found better fitted with a high correlation coefficient ($R^2 = 0.97$ for mixed waste tea and 0.92 for coffee ground) than to Langmuir model ($R^2 = 0.89$ for mixed waste tea and 0.86 for coffee ground) for the 10–250 mg $L^{-1}$ concentration range. Analysis of kinetic studies indicated that Cr(VI) adsorption by both adsorbents was consistent with the pseudo-second-order kinetic model with a good $R^2$ and Marquardt's present standard deviation (MPSD) values. Experimental data demonstrated a sorption capacity of 94.34 mg $g^{-1}$ of mixed waste tea and 87.72 mg $g^{-1}$ of coffee ground. Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and Energy dispersive X-ray spectroscopy (EDS) revealed the noticeable chromium accumulation on the adsorbent surfaces after adsorption. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) studies showed that carbon and oxygen functional groups on the surface of both adsorbents involved in Cr(VI) adsorption. The adsorbents could be reused four times. Large-scale operation using 100 L of packed-bed reactor showed the breakthrough time of adsorption for mixed waste tea of 30 min in 100 mg $L^{-1}$ Cr(VI) concentration. These results suggested that mixed waste tea and coffee ground be considered as alternative adsorbent for Cr(VI) removal.

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## 1. Introduction

Chromium is one of the major heavy metals released to the environment by various industries such as leather production, electroplating, wood preservation and textiles etc. (Mohan and Pittman, 2006). It is mainly present in the environment as trivalent, Cr(III) and hexavalent, Cr(VI) stable oxidation states. The Cr(III) is an essential element in human, plant and animal metabolism (Pressman and Buff, 2000). It is much less toxic than the Cr(VI) form, which is recognized as a carcinogenic and mutagenic agent (IARC, 1987; Whitcare, 2012; Yao et al., 2008). The Cr(VI) is remarkably hazardous and being listed by the United States Environmental Protection Agency (USEPA) as one of the 129 most critical pollutants (Krishnani and Ayyappan, 2006). Human toxicity

of Cr(VI) is ranged from skin irritation to lung cancer, as well as kidney, liver, and gastric damages (Cieslak-Golonka, 1995). The liberated wastewaters from the industries pose a major risk to environment as they are very persistent. The USEPA has announced the maximum permissible limit of Cr(VI) to 0.05 mg $L^{-1}$ (EPA, 1990), while total chromium, including Cr(III), Cr(VI), and its other forms is regulated to below 2 mg $L^{-1}$ (WHO, 2004). Therefore, to reduce the environmental risk of the chromium in industrial wastewater, Cr(VI) should be treated before releasing to the environment. Various treatment technologies have been suggested for the removal of Cr(VI) from wastewater. These include chemical precipitation, membrane-based separation, ion-exchange resins, adsorption, and solvent extraction (Barrera-Díaz et al., 2012; Rengaraj et al., 2001; Song et al., 2004). Adsorption, in comparison with the other methods, is being used extensively for removing heavy metals from aqueous solution. The usefulness of this method lies in the benefits of cleaner and easy controlled process, more efficient and cost-effective technology (Atar et al., 2012; Pintor et al., 2015). However, economical operating cost from the use of low-cost adsorbents is a major concern for a practical deployment. Many by-products of agriculture like sawdust, rice husk, nut and walnut shells, eucalyptus bark, and wheat bran have been investigated as potential adsorbents for the removal of Cr(VI) from wastewater (Ghasemi et al., 2015; Hegazi, 2013; Kaya et al., 2014; Sugashini and Begum, 2015; Sumathi et al., 2005; Xavier et al., 2013). Moreover, Cr(VI) removal using modified biomaterials such as activated carbon from tamarind wood and coconut shell, phosphate treated sawdust, coconut husk and palm pressed fibers, oil palm endocarp, and *Leucaena leucocephala* waste sawdust were documented (Acharya et al., 2009; Ajmal et al., 1996; Babel and Kurniawan, 2004; Malwade et al., 2016; Marrugo et al., 2015; Tan et al., 1993). However, many of these readily available adsorbents showed a limit of adsorption capacity and could not be reused (Table 1). Therefore, it is always of interest to search for new low-cost adsorbents, which is suitable for a practical application in large-scale operation.

Coffee and tea are one of the worldwide-consumed beverages with the average of many billion cups daily, and hence liberating considerable waste. Some waste can be recycled into cosmetic production with remainder unused and, in many occasions, posing a disposal problem. One solution to recycle these wastes is to use them as alternative useful materials. Owing to the facts that coffee ground and waste tea contain oxidizing organic chemicals mainly rich of oxygen and hydroxyl, carboxyl, amino, sulfonic and phenolic functional groups, which are the basic materials involved in adsorption of heavy metals (Ballesteros et al., 2014; Yashin et al., 2015). To overcome the disposal problem, this study aims to apply coffee ground and mixed waste tea as alternative low-cost adsorbents for Cr(VI) removal from synthetic wastewater. The optimal condition for Cr(VI) adsorption was investigated using batch experiments. Equilibrium isotherms and adsorption kinetics were studied. Finally, adsorption efficiency in large-scale operation using a packed-bed reactor was monitored.

## 2. Materials and methods

### 2.1. Synthetic wastewater characteristics

Synthetic wastewater used in this study had similar characteristics as that of municipal wastewater. It consists of tap water together with relative trace concentrations of suspended dissolved organic and inorganic solids: 29.1 g of sucrose, 9.1 g of $CH_3COONa$, 10 g of $NH_4Cl$, 1.8 g of $MgCl_2$, 0.9 g of $CaCl_2 \cdot 2H_2O$, 18.18 g of $NaHCO_3$, 1.19 g of $K_2HPO_4$ and 0.59 g of $KH_2PO_4$ in 40 L of tap water. The resulting characteristics were pH between 6.5 and 7.5, total chemical oxygen demand (TCOD) 812.3 mg COD $L^{-1}$, soluble chemical oxygen demand (SCOD) 721.8 mg COD $L^{-1}$, mixed liquor suspended solids (MLSS) 98 mg $MLSSL^{-1}$ and ammonia nitrogen ($NH_4^+$–N) 53.2 mg $NL^{-1}$.

### 2.2. Preparation and morphological characterization of adsorbents

Two adsorbents, coffee ground and mixed waste tea were kindly received from a coffee shop in Burapha University, Chon Buri, Thailand. They were dried in an oven at 60 °C for 3 d and kept in desiccators until used.

Morphological characterization of the adsorbents was conducted by SEM-EDS (Leo, Eindhoven, Netherlands) and TEM-EDS (JEM-2100, JEOL, Japan) techniques. The SEM samples were cross-section cut and dried under vacuum. Then, the samples were fixed on the stub and sputter-coated with gold particle. The analysis parameters were pressure $1.3 \times 10^{-2}$ Pa and resolution ˂10 nm at 115 kV. For TEM, the samples were isolated by ultrasonically treating the adsorbent in ethanol and drying the residual solvent on carbon-coated copper TEM grids. TEM images were taken using a JEOL JEM-2100 at 200 kV. EDS analysis was done with an Oxford PentaFetx5 probe. The specific surface area of the adsorbents was estimated using a surface area and pore size analyzer (Autosorb 1 MP, Quantachrome) with $N_2$ and the Brunauer-Emmett-Teller (BET) method. The total pore volume was determined as the volume of nitrogen that was kept in the sample at relative pressure, p $p_0^{-1}$ of 0.99.

FTIR (Specac GS01160, USA) was analyzed to investigate the interaction between adsorbent and chromium. The adsorbents were initially dehydrated at 80 °C for 3 h and grinded by agate mortar and pestle. Then, the adsorbents were mixed separately with spectroscopic grade of KBr powder for preparing powder samples and pressed for pellet formation using a 10 tons pressure. The KBr-sample pellets were 13 mm diameter and 1 mm thickness. Finally, the samples were analyzed in the diffuse reflectance mode at a resolution of 4000–400 $cm^{-1}$ under a 4 $cm^{-1}$ resolution. The baseline of raw data was adjusted, and modified data were normalized using OMNIC 8.0.342 software (Thermo Scientific, USA). A change in chemical composition of the adsorbent surface

**Table 1**
Adsorption capacity of mixed waste tea and coffee ground compared to the other published low-cost adsorbents for Cr(VI) removal.

| Adsorbent | Maximum Cr(VI) concentration (mg $L^{-1}$) | pH | Adsorption capacity (mg $g^{-1}$) | Reference |
|---|---|---|---|---|
| Mixed waste tea | 250 | 2 | 94.34 | This study |
| Coffee ground | 250 | 2 | 87.72 | This study |
| Peanut shell | 100 | 4 | 8.31 | Al-Othman et al. (2012) |
| Coconut shell charcoal | 25 | 4 | 10.88 | Babel and Kurniawan (2004) |
| Treated waste newspaper | 50 | 3 | 59.88 | Dehghani et al. (2016) |
| Walnut shell | 100 | 2 | 40.83 | Ghasemi et al. (2015) |
| Fertilizer industry waste | 100 | 4 | 15.24 | Gupta et al. (2010) |
| Rice husk | 100 | 2 | 13.1 | Sugashini and Begum (2015) |
| Tamarind hull-based | 50 | 2 | 81 | Verma et al. (2006) |

was investigated using an XPS (AXIS ULTRA[DLD], Kratos analytical, Manchester, UK.) The base pressure in the XPS analysis chamber was ~$5 \times 10^{-9}$ Torr. The samples were excited with X-ray hybrid mode $700 \times 300\,\mu m$ spot area with a monochromatic Al K$_{\alpha\ 1,2}$ radiations at 1.4 keV. X-ray anode was run at 15 kV, 10 mA and 150 W. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 90° with respect to the normal to the sample surface. The spectra were calibrated using the VISION II software included with the instrument and all spectra were charge corrected by means of the adventitious carbon signal (C1s) and oxygen signal (O1s) at 285 eV and 533 eV, respectively.

### 2.3. Cr(VI) analysis

The Cr(VI) concentration was estimated using a spectrophotometer at 540 nm after complexation with 1,5-diphenylcarbazide under acidic condition (pH $2.0 \pm 0.5$) (APHA, 1989). The standard curve of Cr(VI) was constructed under different concentration of $K_2Cr_2O_7$ ($0-1\,mg\,L^{-1}$). The $R^2$ value is 0.9998. The percentage of removed Cr(VI) was calculated using the following equation:

$$Cr(VI)\ removal\ (\%) = \frac{c_i - c_e}{c_i} \times 100$$

where "$c_i$" is the initial Cr(VI) concentration ($mg\,L^{-1}$) and "$c_e$"is the Cr(VI) concentration after the adsorption reaches equilibrium (mg $L^{-1}$). All experiments were done in triplicate and the averages are reported with standard deviation (SD) values.

### 2.4. Adsorption experiments

Adsorption of Cr(VI) onto the adsorbents was done in a batch mode of operation. The experiments were initially performed in 25 mL of synthetic wastewater (pH 7.0) containing $10\,mg\,L^{-1}$ of Cr(VI) at 30 °C and 150 rpm for 1 h. Physical parameters affecting the adsorption efficiency of Cr(VI) by the adsorbents were studied by varying any one of the parameters and keeping the other parameters constant. The parameters studied were adsorbent dosage ($0-6\,g\,L^{-1}$), solution pH (2.0–11.0), initial Cr(VI) concentration ($5-100\,mg\,L^{-1}$), agitation speed (50–350 rpm with 50 intervals), temperature (15–80 °C with 5 °C intervals) and contact time (20–360 min). The effect of common anions present in wastewater (OH⁻, $SO_4^{2-}$, and Cl⁻) on adsorption of Cr(VI) was also tested. The study was performed separately with each anion of varying strength (0–10 mM) in synthetic wastewater (pH 2.0) containing $50\,mg\,L^{-1}$ of Cr(VI) at optimal condition. Control was done in the same manner without other ions. Each experiment was carried out in triplicate and the averages ± SD reported.

Reusability of the adsorbents for Cr(VI) adsorption was tested using batch system. The experiments were conducted in 25 mL of synthetic wastewater supplementing with $50\,mg\,L^{-1}$ of Cr(VI) at optimal condition for 2 h. After adsorption, each adsorbent was washed with 25 mL of distilled water and collected by centrifugation. Then, the 0.1 M NaOH solution (pH 10.0) was added for desorption of Cr(VI) by shaking at 150 rpm for 1 h. The adsorbents were recovered by centrifugation and the residual concentration of Cr(VI) ions in the solution was measured. The fresh Cr(VI) solution was added to adsorbents for next adsorption-desorption cycle. Each cycle of Cr(VI) adsorption was performed for 2 h at the same condition and Cr(VI) removal was expressed in percentage relative to the original adsorption. Desorption amount was calculated using the following equation:

$$Desorption(\%) = \frac{(V_{des} \times c_{des}) \times 100}{(c_i - c_e)V_{ads}}$$

where "$V_{des}$" is the volume of desorbent used (25 mL), "$c_{des}$" is the final concentration of Cr(VI) in solution after desorption ($mg\,L^{-1}$), "$c_e$" is the equilibrium Cr(VI) concentration after adsorption (mg $L^{-1}$), "$c_i$" is the initial Cr(VI) concentration before adsorption (mg $L^{-1}$), and "$V_{ads}$" is the volume of Cr(VI) solution used for adsorption (25 mL).

### 2.5. Adsorption isotherms

Adsorption isotherms are expressed in terms of a relationship between the concentration of non-adsorbed Cr(VI) and the amount of adsorbent at a constant condition. These explain the adsorption process by providing essential information of the adsorption mechanisms. They are fundamentally required to evaluate the equilibrium data with different important isotherm models. In this study, two parameter isotherm models, Langmuir and Freundlich models were selectively tested with the experimentally obtained equilibrium data (Freundlich, 1906; Langmuir, 1916).

Adsorption capacity of Cr(VI) at equilibrium, $q_e$ ($mg\,g^{-1}$) was calculated using the mass balance as shown in the equation:

$$q_e = \frac{(c_i - c_e)}{m} V$$

where "$c_i$" and "$c_e$" are the initial and equilibrium Cr(VI) concentration ($mg\,L^{-1}$), respectively, $q_e$ is the equilibrium adsorption capacity ($mg\,g^{-1}$), m is the mass of adsorbent (g), V is the volume of solution (L).

### 2.6. Adsorption kinetic studies

In this study, two kinetic models were tested to describe the reaction in order of Cr(VI) adsorption. There are pseudo-first-order kinetic and pseudo-second-order kinetic models (Qiu et al., 2009). Moreover, an intra-particle diffusion model was also analyzed (Hameed and Ahmad, 2009). The experiments were conducted by adsorption of Cr(VI) on mixed waste tea and coffee ground at optimal condition: pH 2.0, agitation speed 250 rpm, 30 °C, $2\,g\,L^{-1}$ of the adsorbent, contact times in the range of 20–360 min with different initial Cr(VI) concentrations.

The best fit of kinetic model to the experimental data was estimated according to regression coefficient values ($R^2$) obtained from a linear plot of the equation model and the MPSD value developed by Marquardt (1963). The MPSD value was calculated using the following equation:

$$MPSD = 100 \left( \sqrt{\frac{1}{p-n} \sum_{i=1}^{p} \left[ \frac{q_{t,\exp} - q_{t,calc}}{q_{t,\exp}} \right]_i^2} \right)$$

where "p" is the number of the experimental data point and "n" is the number of parameters of the model equation. "$q_{t,\exp}$" and "$q_{t,calc}$" are referring to experimental and calculated values from model equation, respectively.

### 2.7. Packed-bed reactor

Packed-bed reactor was constructed as column using empty-refillable water filter cartridge (size; $2.5'' \times 10''$). Two hundred grams of mixed waste tea was packed in the reactor. Fig. S1 shows the model of packed-bed reactor used in this study. The adsorption

studies were carried out with a working volume of 100 L synthetic wastewater. The initial Cr(VI) concentrations supplementing in the synthetic wastewater were varied in the range of 40–100 mg L$^{-1}$. System was operated at optimum pH and room temperature (28–30 °C). The initial flow rate of water feeding was fixed at 300 mL min$^{-1}$ by Diaphragm booster pump (DEW, Italy) and running time was 4 h.

## 3. Results and discussion

### 3.1. Adsorbent characteristics

Waste tea and coffee ground are big deposit beverage wastes, liberating global disposal problem. In this study, mixed waste tea and coffee ground from coffee shops in Burapha University were selected as alternative adsorbent for investigation of Cr(VI) removal. The mixed waste tea contains 47.36% carbon, 44.03% oxygen, 4.68% potassium, 2.13% calcium and trace levels of magnesium, aluminium and chromium (Fig. S2a). SEM image indicates smooth surface and compose of the agglutinative flakes of original waste tea. In the same way, the EDS analysis of coffee ground (Fig. S2c) mainly represented the percentage of carbon and oxygen as 35.48% and 58.06%, respectively. Other atomic components showed percentage by weight <2.5%. The smooth and thin layer surface was also detected as shown in the SEM image. Trace levels of chromium found in both mixed waste tea and coffee ground are possibly due to the original contamination occurred during tea or coffee growth, transportation, packaging, and processing. Many documents confirmed the presence of chromium in tea and coffee (Amin and Kassem, 2012; Mandiwana et al., 2011; Seenivasan et al., 2008; Zaleschi et al., 2012). Based on the results for the BET surface area, mixed waste tea and coffee ground has an area of 13.86 m$^2$ g$^{-1}$ and 13.01 m$^2$ g$^{-1}$, respectively. Total pore volume of mixed waste tea was 0.0173 cm$^3$ g$^{-1}$, which is similar to the total pore volume in coffee ground (0.0177 cm$^3$ g$^{-1}$). The average pore diameter of mixed waste tea and coffee ground was 4.99 nm and 5.44 nm, respectively, suggesting a mesoporous structure (Zdravkov et al., 2007).

Although the adsorption mechanism of heavy metal especially Cr(VI) by waste tea and coffee ground is still not documented. There are some reports suggesting biosorption of heavy metal by these materials uses carboxyl and amine groups for binding (Ahluwalia and Goyal, 2005). Also, some reports described cellulose and hemicellulose, lignin and condensed tannins as responsible functional groups for metals adsorption by waste tea (Nandal et al., 2014). Thus, to investigate the possibility of waste tea and coffee ground as alternative adsorbent for Cr(VI) adsorption, FTIR analysis

was performed. The infrared spectra of the adsorbents are illustrated in Fig. S3. The more intense spectra frequencies are reported in Table 2. Both mixed waste tea and coffee ground have considerable numerous functional groups where there was good possibility for Cr(VI) to be adsorbed. For examples, the functional groups OH, NH and CH stretching in alcohol or amine or alkyl existed in mixed waste tea and coffee ground at wavenumber 3445 cm$^{-1}$ or 3446 cm$^{-1}$. The CH stretching in alkane was also detected in both adsorbents at wavenumber 2852-2915 cm$^{-1}$ for mixed waste tea and 2848-2923 cm$^{-1}$ for coffee ground while amino groups were found at wavenumber 2339-2360 cm$^{-1}$. These are similar with the results of Gorzin and Ghoreyshi (2013) and Mulani et al. (2013) which the OH groups and CH stretching of alkanes were presented in waste tea and coffee ground used for Cr(VI) adsorption. The C=O groups and C–H bending (in plane) were identified at wavenumber 1465-1645 cm$^{-1}$ for mixed waste tea and 1460-1700 cm$^{-1}$ for coffee ground. The C–O stretching for aliphatic amines (1070 cm$^{-1}$) and N–H bending (1558-1645 cm$^{-1}$) were also noticed in the adsorbents. There were reports about the involvement of C=O groups and −NH group in Cr(VI) adsorption by many modified biomaterials (Bai and Abraham, 2002; Levankumar et al., 2009; Teymouri et al., 2013; Xining et al., 2015). Thus, it can be noted here that mixed waste tea and coffee ground would be applicable candidate adsorbent for the Cr(VI) removal.

### 3.2. Optimization of adsorption condition

#### 3.2.1. Effect of adsorbent dosage

Various factors affecting the adsorption as well as the complexation of chromium ions were investigated. Removal of Cr(VI) at the initial concentration of 10 mg L$^{-1}$ was firstly tested in synthetic wastewater (pH 7.0) for 1 h at 30 °C and 150 rpm, with different doses of the absorbent used. This examination is vital to get the trade-off between the adsorption capacity and the percentage removal of Cr(VI) resulting in an optimum adsorbent dosage. As shown in Fig. S4a, the %Cr(VI) removal are similar (~30%) when 0.5–2 g L$^{-1}$ of coffee ground were applied. Then, the removal efficiency was gradually increased by increasing the coffee ground dose and seemed to be constant at the dosage between 5 and 6 g L$^{-1}$. For mixed waste tea, the %Cr(VI) removal was continuously increased and reached maximum (~70%) when 5–6 g L$^{-1}$ was used. These can be explained because for a fixed initial Cr(VI) concentration, an increase in the amount of adsorbent had provided a greater surface area (Khosravi et al., 2014). Overlapping and unsaturation of adsorbent sites limited the adsorption potential at higher amount of the adsorbent used (Jain et al., 2009). Of these, dosage at 5 g L$^{-1}$ of both adsorbents seemed to be optimum.

**Table 2**
FTIR adsorption frequencies of mixed waste tea and coffee ground after Cr(VI) adsorption compared with before adsorption.

| Mixed waste tea | | | Coffee ground | | | Assignment |
|---|---|---|---|---|---|---|
| Main observed bands (cm$^{-1}$) | | | Main observed bands (cm$^{-1}$) | | | |
| Before Cr(VI) adsorption | After Cr(VI) adsorption | Differences | Before Cr(VI) adsorption | After Cr(VI) adsorption | Difference | |
| 3445 | 3446 | −1 | 3446 | 3446 | 0 | OH, NH, CH stretching in alcohol or amide or alkyl |
| 2915 | | | 2923 | 2919 | 4 | CH stretching in alkane |
| 2852 | | | 2848 | 2846 | 2 | |
| 2360 | 2360 | 0 | 2360 | 2360 | 0 | Amino groups |
| 2339 | 2341 | −2 | 2340 | 2339 | 1 | |
| | 1700 | | 1700 | 1700 | 0 | C=O groups, C−H bending and N−H |
| 1645 | 1649 | −4 | 1653 | 1653 | 0 | bending |
| 1558 | 1558 | 0 | 1558 | 1560 | −2 | |
| 1465 | 1445 | 20 | 1460 | 1463 | −3 | |
| — | — | — | 1070 | 1074 | −4 | C−O stretching for aliphatic amines |

However, high chemical oxygen demand (COD) values (>2000 mg L$^{-1}$) were detected in effluent after adsorption when >2 g L$^{-1}$adsorbents were used. Thus, to overcome this unsatisfied problem, 2 g L$^{-1}$of both adsorbents should be a sufficient dose for Cr(VI) removal and were selected as optimum dosage for the next studies.

### 3.2.2. Effect of pH

Solution pH is another significant parameter influence on the adsorbent surface charge and degree of ionization. Adsorption of Cr(VI) on both adsorbents gave a similar pattern which strongly depends on the initial pH (Fig. S4b). Maximum Cr(VI) removal (95.08% for mixed waste tea and 85.25% for coffee ground) was achieved at pH 2.0. Increase in the solution pH had progressively decreased the removal efficiency. This could clarify by the fact that Cr(VI) has different ionic forms ($H_2CrO_4$, $HCrO_4^-$, $CrO_4^{2-}$ and $Cr_2O_7^{2-}$) in the aqueous solution and the stability of these ions mainly depends on the solution pH. At strong acidic pH, $HCrO_4^-$ is the dominant Cr(VI) species easily bound to the positive charged adsorbents by means of electrostatic interaction. But at higher pH, competitiveness of $CrO_4^{2-}$ and $OH^-$ ions interfere the binding site on the adsorbents (Baral et al., 2006; Suksabye and Thiravetyan, 2012). Thus, pH 2.0 was selected as optimum pH for next studies. Maximum adsorption efficiency at acidic pH recommends the potential of these adsorbents for decontamination of Cr(VI) from wastewater, especially the effluent from chrome tanning that pH 3.5 was recorded (Islam et al., 2014).

### 3.2.3. Effect of agitation speed

In this study, agitation speed was varied between 50 and 350 rpm and keeping adsorbent dosage and pH constant. As shown in Fig. S4c, the %Cr(VI) removal by both adsorbents increased by increasing of agitation speed and seemed to be constants at the speed >250 rpm. Using of mixed waste tea gave adsorption efficiency ~95% at 200–350 rpm while the Cr(VI) removal >80% was obtained from coffee ground at the speeds 250–350 rpm. These might due to improvement of the degree of physico-chemical interaction between Cr(VI) ions and negatively charged of the adsorbents as well as higher diffusion of the chromium ions towards the adsorbent surface (Babel and Kurniawan, 2004). Throughout the results, the speed at 250 rpm was recommended as the optimum agitation speed for Cr(VI) adsorption and used in further experiments.

### 3.2.4. Effect of contact time

The effect of contact time on Cr(VI) adsorption by mixed waste tea and coffee ground was investigated over the time. Almost complete adsorption (~97%) was detected after 80 min for both adsorbents (Fig. S4d and Fig. S4e). A quick removal of Cr(VI) was found in the early stages of the adsorption process. Then, the percentages of Cr(VI) removal were slowly increased and tended to attain equilibrium at 100 min and 120 min for mixed waste tea and coffee ground, respectively. It can be noted that during the initial stage of the adsorption process, the higher concentration of Cr(VI) ion provide the diving force to facilitate ion diffusion from solution to surface of adsorbent. Moreover, increase of contact time promotes sufficient time for Cr(VI) ions attached with the adsorbent surface. Slower rate of Cr(VI) adsorption before equilibrium possibly due to occupation of the adsorbent surface and the decrease of Cr(VI) ion concentration, leads to a decrease in uptake rate until equilibrium is achieved. Another reason might be the electrostatic hindrance or repulsion between the adsorbed Cr(VI) ions and the adsorbent surface (Nemr, 2009; Verma et al., 2006). Hence, according to the results, the contact time as 120 min was selected for further studies.

### 3.2.5. Effect of temperature

Adsorption experiments were performed in the temperature range of 15–80 °C (Fig. S4f). Using of mixed waste tea as the adsorbent revealed similar percentage of Cr(VI) removal at all studied temperature except at beyond 25 °C and above 65 °C that the efficiency was 10–20% decreased. These could be concluded that there is no internal bond breakage near the edge of the adsorbent active surface sites (Ucun et al., 2008). Adsorption efficiency of Cr(VI) using coffee ground was rapidly increased with further increase of temperature from 15 °C to 45 °C. These suggest the Cr(VI) adsorption process is endothermic in character (Kara and Demirbel, 2012). Maximum adsorption (~95%) was observed at 50–65 °C and then slightly decreased but still >80% removal. High removal percentages of Cr(VI) at wide temperature range recommends the potential of these wastes as alternative adsorbent for decontamination of Cr(VI) from industrial effluents.

### 3.2.6. Effect of initial Cr(VI) concentration

Almost complete adsorption of Cr(VI) was observed for initial Cr(VI) concentration up to 40 mg L$^{-1}$ and 35 mg L$^{-1}$ for mixed waste tea and coffee ground, respectively (Fig. S4g). As expected, the removal efficiency decreased when initial concentration of Cr(VI) continuously increased. These might due to limited of surface area to be adsorbed (Owalude and Tella, 2016). However, high percentages of Cr(VI) removal (80–90%) were still recorded at the concentration up to 80 mg L$^{-1}$. At 100 mg L$^{-1}$ of Cr(VI) concentration, coffee ground showed a better performance of adsorption than mixed waste tea ~20%.

### 3.2.7. Effect of other ions

Three anions, $OH^-$, $SO_4^{2-}$ and $Cl^-$, commonly found in wastewater with varying strength were tested along with a control (without anion). Two of them ($Cl^-$ and $SO_4^{2-}$) did not show any inhibitory effect on Cr(VI) adsorption (Table S1). The %Cr(VI) removal decreased by 10% possibly due to desorption effect of $OH^-$ (Gorzin and Abadi, 2018).

### 3.3. Reusability of the adsorbents

The potential of adsorbent to be reused is the key factor for practical uses of the adsorbent with cost effective. Studies were performed in synthetic wastewater containing 50 mg L$^{-1}$ Cr(VI) at optimal condition. After adsorption, the adsorbents were washed with 0.1 M NaOH and dried at 60 °C for 24 h before being used in the next cycle. As shown in Fig. S5, a slight drop of %Cr(VI) removal was recorded in the second cycle for both mixed waste tea and coffee ground. More than 50% of Cr(VI) removal remained in the third and fourth cycle while 20–30% of Cr(VI) removal was detected in the fifth cycle. These results support the fact that adsorption process of Cr(VI) is reversible (Tytłak et al., 2015) which desorption of Cr(VI) occurred by the action of NaOH (Gorzin and Abadi, 2018). Moreover, the results showed that 10–15% of desorbed chromium was in the form of Cr(VI). These indicate conversion of Cr(VI) to other valence forms after adsorption. The decrease in %Cr(VI) removal possibly due to a progressive saturation of the binding Cr(VI) ions with negative charge of functional group in active site of the adsorbent or extreme pH conditions might destroy textural characteristics of the adsorbent. In addition, impurities from the reaction process such as salts from synthetic wastewater and heavy metal contaminants of untreated adsorbent probably block the active surfaces of the adsorbent (Kyzas, 2012).

### 3.4. Morphological and physical changes of the adsorbent after Cr(VI) adsorption

After adding the mixed waste tea or coffee ground in synthetic wastewater containing $50\,mg\,L^{-1}$ Cr(VI) at optimal condition, both adsorbents became shiny and coarse surface (Fig. S2c and Fig. S2d). These results are in well agreement with that of the SEM-EDS analysis representing chromium accumulation on adsorbent surfaces. The percentage of chromium as 24.79% and 23.91% was detected on the surface of mixed waste tea and coffee ground, respectively after adsorption. By combining the results with TEM images and EDS analysis, it is clearly shown that chromium can be accumulated on the adsorbent surface after adsorption (Fig. S6).

The FTIR spectra of mixed waste tea and coffee ground after adsorption are illustrated in Fig. S3c and S3d. Comparisons of intense frequencies before and after adsorption are summarized in Table 2. The FTIR spectrum of mixed waste tea shows that some peaks were shifted or disappeared ($2915\,cm^{-1}$ and $2852\,cm^{-1}$) and new peaks were detected ($1700\,cm^{-1}$). These changes suggest the possible stretching vibrations of CH groups on the surface of mixed waste tea after Cr(VI) adsorption (Ahmad et al., 2013; Kaya et al., 2016). However, no significant changes on either the position or intensity during Cr(VI) adsorption by coffee ground could be detected. Then, XPS analysis was performed in parallel to identify the chemical change.

The XPS survey spectra (Fig. S7) indicates that carbon and oxygen are main elements on the adsorbent surface. However, there is no chromium signal in the spectra after adsorption. This implies binding of Cr(VI) to the surface of adsorbents possibly occurred via the carbon and oxygen functional groups (Li et al., 2008; Sawalha et al., 2007). The XPS spectra corresponding to the C1s and O1s narrow scan region of the adsorbents before and after adsorption of Cr(VI) were compared (Fig. 1). The XPS C1s spectrum of mixed waste tea after Cr(VI) adsorption (Fig. 1a) shows the shift of component peaks corresponding to graphitic carbon (C–C) or carbogen (C–H, B.E. = 285.06 eV, 73.7%) and hydroxyl/ether groups (C–O, B.E. = 286.15 eV, 10%). Similarly, after Cr(VI) adsorption, the shift of peaks corresponding to graphitic carbon (C–C) or carbogen (C–H, B.E. = 284.98 eV, 76.6%), hydroxyl/ether groups (C–O, B.E. = 286.00 eV, 8%), and carbonyl/carboxy groups (C=O/O–C–O, B.E. = 286.85 eV, 8%) were found in coffee ground (Fig. 1c). For XPS O1s spectrum (Fig. 1b and c), the shift peaks of carbonyl/carboxy groups as well as hydroxyl/ether groups were also displayed for both adsorbents after adsorbed with Cr(VI). These can be noted here that both adsorbents use carbon and oxygen functional groups on the surface for Cr(VI) adsorption.

### 3.5. Time-course monitoring of Cr(VI) adsorption with different initial concentrations

The adsorption of Cr(VI) by mixed waste tea and coffee ground were time-course studied in synthetic wastewater containing different initial Cr(VI) concentrations ($10-250\,mg\,L^{-1}$) at optimal condition and 30 °C. Similar pattern of adsorption efficiency was observed from both adsorbents (Fig. S8). The removal efficiency of Cr(VI) increased parallel with the increase of contact time. At low concentrations of Cr(VI), mixed waste tea showed complete adsorption within 80 min and 180 min of contacting time when $10\,mg\,L^{-1}$ and $20-30\,mg\,L^{-1}$ of Cr(VI) was used, respectively (Fig. S8a) while coffee ground totally adsorbed $10\,mg\,L^{-1}$ Cr(VI) after 140 min (Fig. S8b). Maximum removal level was constantly detected after 180 min for mixed waste tea and 240 min for coffee ground when higher initial Cr(VI) concentrations were used. These times were considered as the equilibrium response time which indicates that the adsorption was saturated with Cr(VI) ions. The rapid rate of adsorption in the initial stages of the process probably
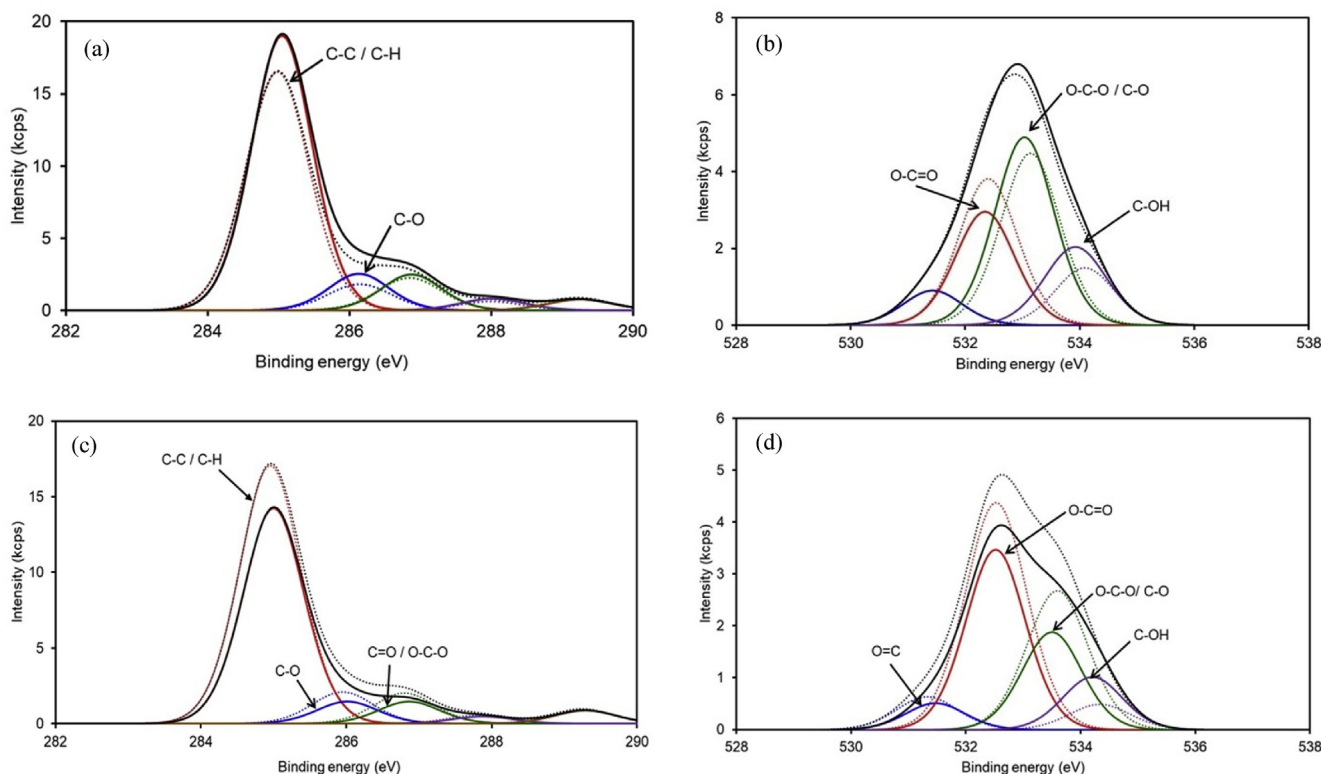


**Fig. 1.** Comparison of XPS spectra of mixed waste tea and coffee ground before and after Cr(VI) adsorption. High-resolution spectra of (a) C1s of mixed waste tea, (b) O1s of mixed waste tea, (c) C1s of coffee ground, and (d) O1s of coffee ground.

**Table 3**
Isotherm parameters for Cr(VI) adsorption onto mixed waste tea and coffee ground.

| Adsorbent | Langmuir parameters | | | | Freundlich parameters | | | |
|---|---|---|---|---|---|---|---|---|
| | $K_L$ (calculated) (L mg$^{-1}$) | $R_L$ (L mg$^{-1}$) | $q_m$ (mg g$^{-1}$) | $R^2$ | $K_f$ (calculated) (mg g$^{-1}$) | 1/n | n | $R^2$ |
| Mixed waste tea | 0.10 | 0.037–0.082 0<$R_L$<1 | 97.09 | 0.8905 | 20.05 | 0.31 | 2.06 | 0.9723 |
| Coffee ground | 0.12 | 0.031–0.072 0< $R_L$ < 1 | 87.72 | 0.8600 | 23.15 | 0.39 | 3.24 | 0.9233 |

due to the availability of abundance adsorption site of the adsorbents used for Cr(VI) binding. In the same way, slow rate of adsorption comes from limited of adsorbent capacity at the equilibrium (Kumar et al., 2008). Thus, the equilibrium adsorption at 360 min was used to calculate the isotherm and kinetic adsorption.

### 3.6. Adsorption isotherm

The Langmuir and Freundlich isotherm models were used to describe the equilibrium relationship between Cr(VI) and adsorbents (mixed waste tea and coffee ground).

#### 3.6.1. Langmuir model

The linear Langmuir isotherm plots of mixed waste tea and coffee ground are shown in Fig. S9. Moderate values of correlation coefficient ($R^2 = 0.89$ for mixed waste tea and $R^2 = 0.86$ for coffee ground) as presented in Table 3 indicate that Langmuir isotherm was unsuitable for Cr(VI) adsorption onto these adsorbents. Maximum adsorption capacities ($q_m$) of 97.09 mg g$^{-1}$ for mixed waste tea and 87.72 mg g$^{-1}$ for coffee ground were exhibited.

The main characteristic of Langmuir equation is a dimensionless constant called equilibrium parameter ($R_L$) which indicates the type of isotherm. $R_L > 1$ is unfavorable and used for non-optimum adsorption, $R_L = 1$ is linear adsorption, $0 < R_L < 1$ is favorable and used for optimum adsorption and $R_L = 0$ is irreversible adsorption. According to the obtained results, mixed waste tea showed 0.037–0.082 $R_L$ values and the $R_L$ values of 0.031–0.072 were found by coffee ground. These indicate optimum adsorption of Cr(VI)

under study condition.

#### 3.6.2. Freundlich model

The linear form of Freundlich model equation is reported in Fig. S9. A good correlation ($R^2 > 0.9$) between the experimental data and Freundlich adsorption models for Cr(VI) suggests that both mixed waste tea and coffee ground possess high sorption capacity and high affinity for Cr(VI) (Table 3). As 1/n indicates type of adsorption process: $1/n = 0$ is irreversible process, $0 < 1/n < 1$ is optimum adsorption state and $1/n > 1$ non-optimum adsorption or cooperative adsorption. Our result showed $1/n = 0.31$ for mixed waste tea and $1/n = 0.39$ for coffee ground which lies between 0 and 1 indicates favorable adsorption. The Freundlich isotherm constant ($K_f$) were calculated as 20.05 mg g$^{-1}$ for mixed waste tea and 23.15 mg g$^{-1}$ for coffee ground. Thus, from the results, the adsorption of Cr(VI) onto mixed waste tea and coffee ground fitted well with the Freundlich isotherm model, which indicates that Cr(VI) uptake occurs on heterogeneous surface by multilayer adsorption (Malik, 2004; Owalude and Tella, 2016).

### 3.7. Adsorption kinetic studies

The study of adsorption kinetics which describes the rate of adsorption is the key factor used for designing a process. The adsorption kinetic depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process (Wang et al., 2005). Experimental data were used to predict the kinetics chromium adsorption. In this study, the adsorption data
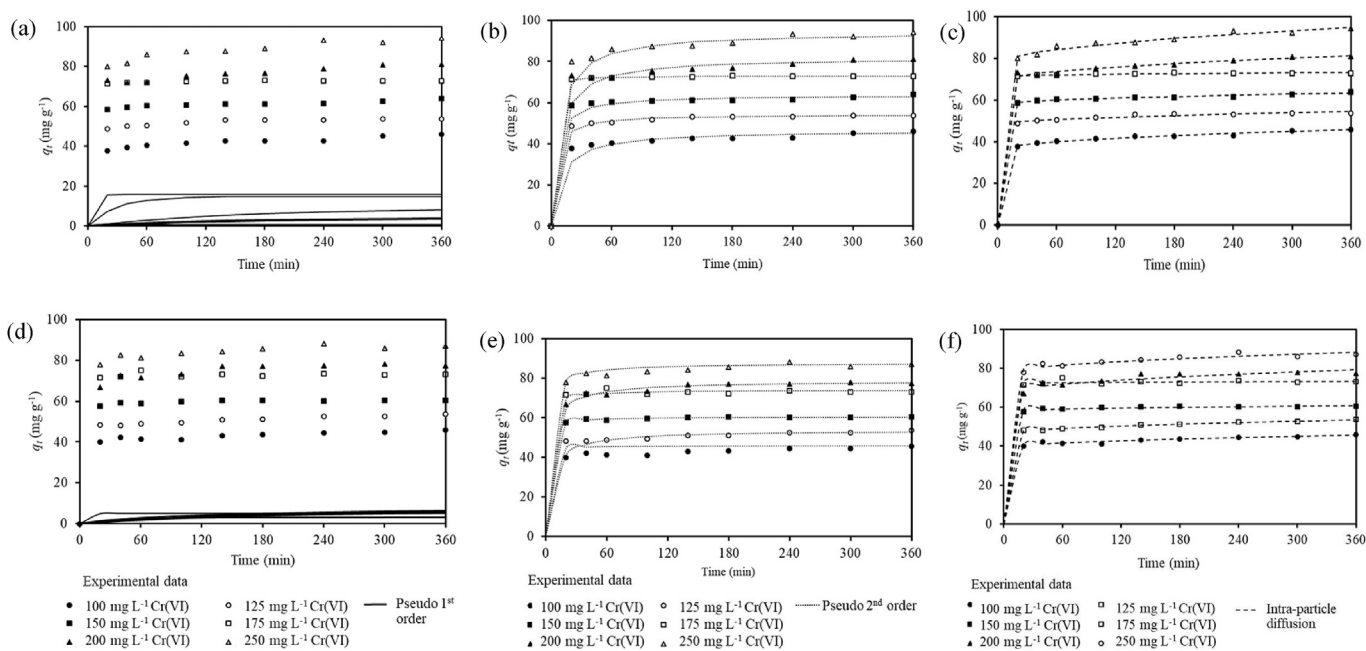


**Fig. 2.** Kinetic plots for adsorption of Cr(VI) onto (a–c) mixed waste tea and (d–f) coffee ground at 100–250 mg L$^{-1}$ Cr(VI) concentrations. (a, d) Pseudo-first-order model, (b, e) Pseudo-second-order model, (c, f) Intra-particle diffusion models. Symbols represent the experimental data and linear/dot/dash lines imply theoretical data fitting of the model. Experimental conditions were pH 2.0, agitation speed 250 rpm, 30 °C, 2 g L$^{-1}$ of adsorbent.

was analyzed with two kinetic models, i.e., pseudo-first-order and pseudo-second-order kinetic models as well as the intra-particle diffusion model. The conformity between experimental data and the model predicted values was expressed by the correlation co-efficients ($R^2$ values closeness to 1) as well as closeness of values between experimental and calculated adsorption capacity values as indicate as MPSD values.

### 3.7.1. Pseudo-first-order model

This model is based on the fact that the change in Cr(VI) ion concentration with respect to time is proportional to be power one. The results of the pseudo-first-order adsorption kinetic are plotted in Fig. 2 and Fig. S10. It has been found that the amount of adsorbed Cr(VI) ions onto both adsorbents increase slightly at all studied times. The adsorption uptake, $q_t$ (mg g$^{-1}$) increases with increased initial concentration and the adsorption rate declines and reaches the equilibrium position over time. However, the experimental data are far from the theoretical data. The linear form of the model was used for model prediction. Values of $k_1$ (pseudo-first-order rate constant) are calculated from the plots of log ($q_e$-$q_t$) versus t (Fig. S11 and S12). The $R^2$ values obtained for mixed waste tea and coffee ground are shown in Table 4. These values are relatively small and the experimental $q_e$ values do not agree with the values calculated from the linear plot. High MPSD values confirming a big gap of $q_t$ values between experiments and theories were also found. These suggest the pseudo-first-order kinetic model is not well fitted to the data obtained from the studies.

### 3.7.2. Pseudo-second-order model

The pseudo-second-order model, an indication of a chemi-sorptions mechanism was also analyzed. Nonlinear plots of the model are shown in Fig. 2. The plots showed good agreement between theoretical and experimental data of the pseudo-second-order model. The kinetic rate of adsorption can be predicted using a linear form equation of the model. The plot t/$q_t$ against t as shown in Fig. S11 and S12 presented straight line with slope of 1/$k_2 q_e^2$ and intercept of 1/$q_e$, the constants ($q_e$ and $k_2$) as experimentally determined from the plot are summarized in Table 4. According to the results, the pseudo-second-order kinetics model

gave a larger correlation coefficient ($R^2 > 0.99$) and close in values between $q_{e, exp}$ and $q_{e, cal}$. The smallest correlation coefficient in this case was 0.991, which is still better than the pseudo-first-order kinetic model. The MPSD values < 10 indicate a closeness of $q_{e,exp}$ and $q_{e, cal}$. These data recommended the adsorption of Cr(VI) onto mixed waste tea and coffee ground was consistent with the pseudo second-order kinetic model. Hence, it can be concluded that chemical adsorption (chemisorptions) is the rate-limiting step. A similar conclusion has been documented for the adsorption of Cr(VI) by tamarind wood (Acharya et al., 2009) and cereal by-products (Arris et al., 2016). The adsorption of heavy metals onto waste tea was also consistency reported (Ghasemi et al., 2017).

### 3.7.3. Intra-particle diffusion model

Since transportation of Cr(VI) ions to the surface of the adsorbent might occur in several steps: film or external diffusion, pore diffusion, surface diffusion and the adsorption on the pore surface, or a combination of more than one step. Also, in a rapidly stirred batch adsorption, the diffusive mass transfer can be related by an apparent diffusion coefficient. The Morris-Weber equation is generally applied to evaluate the intra-particle diffusion rate constant ($k_{id}$). Fig. 2 show a plot $q_t$ against time of the diffusion model. The linear portion of the plot $q_t$ vs $t^{0.5}$ (Fig. S11 and Fig. S12) for a wide range of contact time between Cr(VI) ions and adsorbents (mixed waste tea and coffee ground) do not pass through the origin. This might due to difference in the rate of mass transfer between the initial and final stages of adsorption. Furthermore, such deviation from the origin indicated that the intra-particle diffusion is not only the rate-limiting step. Although the correlation co-efficients ($R^2$) for this model (Table 4) are higher than those obtained from pseudo-first-order kinetic model, the $R^2$ values of pseudo-second-order kinetic model are more closeness to 1. Thus, the experimental data fit better to the pseudo-second-order kinetic model than the other two models.

From all results, the mechanism of Cr(VI) adsorption by both adsorbents can be proposed. At first, the Cr(VI) attaches to adsorbent using chemical interaction, possibly by the carboxyl/carbonyl groups on the adsorbent surface. Then, multilayer adsorption as film covering the adsorbent surface occurred before reduction to

**Table 4**
Kinetic constants for Cr(VI) adsorption onto mixed waste tea and coffee ground.

| Adsorbent | Experimental | | Kinetic model constants, $R^2$ and MPSD | | | | | | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | Pseudo-first-order model | | | | Pseudo-second-order model | | | | Intra-particle diffusion model | | | |
| | Cr(VI) (mg L$^{-1}$) | $q_e$ (exp.) (mg g$^{-1}$) | $q_e$ (cal.) (mg g$^{-1}$) | $k_1$ (min$^{-1}$) | $R^2$ | MPSD | $q_e$ (cal.) (mg g$^{-1}$) | $k_2$ (min$^{-1}$) | $R^2$ | MPSD | $k_{id}$ (min$^{-1}$) | $\Theta$ | $R^2$ | MPSD |
| Mixed waste tea | 10 | 4.99 | 10.41 | 0.0111 | 0.5234 | 95.64 | 5.02 | 0.1773 | 1.0000 | 1.01 | 0.0145 | 4.7661 | 0.7137 | 1.31 |
| | 20 | 10.00 | 1.05 | 0.0071 | 0.7398 | 125.83 | 10.04 | 0.0225 | 0.9998 | 2.07 | 0.0818 | 8.5673 | 0.8250 | 3.17 |
| | 30 | 14.97 | 1.68 | 0.0150 | 0.9483 | 122.53 | 15.13 | 0.0195 | 0.9990 | 1.64 | 0.1080 | 13.2200 | 0.8146 | 2.55 |
| | 50 | 24.97 | 5.60 | 0.0147 | 0.9483 | 125.19 | 25.32 | 0.0064 | 0.9990 | 6.77 | 0.2079 | 21.3030 | 0.8997 | 2.12 |
| | 100 | 45.93 | 8.89 | 0.0064 | 0.8658 | 119.08 | 46.30 | 0.0313 | 0.9980 | 8.44 | 0.5144 | 36.0200 | 0.9538 | 1.71 |
| | 125 | 53.78 | 8.89 | 0.0074 | 0.6092 | 128.37 | 54.35 | 0.0030 | 0.9990 | 2.61 | 0.3450 | 47.9350 | 0.8867 | 1.50 |
| | 150 | 63.96 | 8.89 | 0.0039 | 0.9046 | 129.58 | 63.69 | 0.0148 | 0.9940 | 5.05 | 0.3024 | 57.5660 | 0.9205 | 0.92 |
| | 175 | 72.81 | 1.62 | 0.0083 | 0.6092 | 133.04 | 72.99 | 0.0087 | 1.0000 | 0.39 | 0.0999 | 71.2930 | 0.7309 | 0.53 |
| | 200 | 81.05 | 14.77 | 0.0345 | 0.9695 | 110.98 | 81.97 | 0.0028 | 0.9993 | 8.45 | 0.6671 | 68.4620 | 0.9409 | 0.14 |
| | 250 | 94.22 | 15.78 | 0.0078 | 0.8738 | 110.05 | 94.34 | 0.0029 | 0.9992 | 6.79 | 0.9443 | 76.8730 | 0.9402 | 0.73 |
| Coffee ground | 10 | 5.00 | 5.60 | 0.0069 | 0.7180 | 60.83 | 5.05 | 0.0636 | 0.9990 | 3.10 | 0.0482 | 4.2358 | 0.7367 | 4.39 |
| | 20 | 9.91 | 2.78 | 0.0048 | 0.6629 | 116.07 | 10.02 | 0.0174 | 0.9992 | 2.78 | 0.1191 | 7.8865 | 0.8623 | 3.84 |
| | 30 | 14.97 | 1.48 | 0.1244 | 0.8737 | 120.59 | 17.36 | 0.0031 | 0.9970 | 18.52 | 0.0925 | 13.432 | 0.9175 | 1.95 |
| | 50 | 23.98 | 4.00 | 0.0193 | 0.8167 | 115.12 | 24.04 | 0.0081 | 0.9930 | 5.07 | 0.2168 | 19.974 | 0.9175 | 2.04 |
| | 100 | 45.78 | 6.09 | 0.0058 | 0.9199 | 124.51 | 45.87 | 0.0022 | 0.9910 | 9.44 | 0.3568 | 38.727 | 0.8949 | 1.86 |
| | 125 | 53.63 | 6.80 | 0.0062 | 0.9588 | 124.62 | 53.76 | 0.0051 | 0.9940 | 7.14 | 0.3938 | 45.968 | 0.9691 | 0.98 |
| | 150 | 60.44 | 5.12 | 0.1658 | 0.4665 | 122.69 | 60.61 | 0.0037 | 1.0000 | 0.57 | 0.1565 | 57.8570 | 0.7296 | 0.12 |
| | 175 | 73.02 | 3.00 | 0.0299 | 0.5580 | 129.31 | 74.07 | 0.0272 | 0.9960 | 2.76 | 0.0506 | 72.2460 | 0.0536 | 1.82 |
| | 200 | 77.42 | 5.39 | 0.0131 | 0.5958 | 127.19 | 78.74 | 0.0017 | 0.9998 | 2.72 | 0.6671 | 66.6760 | 0.8035 | 2.91 |
| | 250 | 87.10 | 7.19 | 0.0064 | 0.8752 | 127.96 | 87.72 | 0.0014 | 0.9996 | 2.41 | 0.5973 | 76.9660 | 0.8196 | 1.95 |

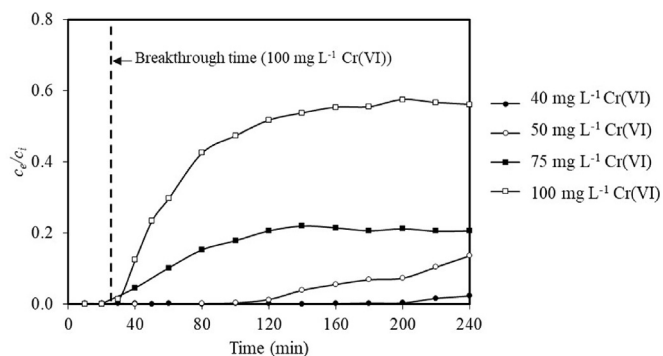**Fig. 3.** Breakthrough curves for Cr(VI) adsorption onto mixed waste tea at different initial feed concentrations.

the other forms of chromium.

### 3.8. Packed-bed reactor study

Based on the kinetic and equilibrium results, there is an evident of Cr(VI) ion on the adsorbents (mixed waste tea and coffee ground) taking place via a multilayer adsorption process. Further continuous fixed bed adsorption should be tested. Mixed waste tea was selected as the model of adsorbent. A 100 L of packed-bed reactor was constructed using empty-refillable water filter filled with 200 g of mixed waste tea. Cr(VI) adsorption was continuously operated for 4 h with different feed concentrations of chromium ($40–100 \, mg \, L^{-1}$) in synthetic wastewater. Experiments were carried out under room temperature ($28–30 \, °C$), pH 2.0 and $300 \, mL \, min^{-1}$ of initial flow rate.

The performance of mixed waste tea in packed-bed reactor modes can be assessed by plotting breakthrough curve. The breakthrough curves obtained from the reactor at different Cr(VI) concentrations are presented in Fig. 3. This can be said that the uptake of Cr(VI) ions decreased with increasing feed concentration. This might due to the increasing availability of Cr(VI) ion to be adsorbed on the active surface of mixed waste tea. The breakthrough time of adsorption for mixed waste tea could be estimated as 30 min for $100 \, mg \, L^{-1}$ of Cr(VI) used. This result strongly suggests an application of mixed waste tea as potential adsorbent for Cr(VI) removal since big amount of Cr(VI) was completely removed in short time of operation using a cost-effective reactor (total operation cost is less than 100 US dollar).

### 4. Conclusion

This study shows the potential of mixed waste tea and coffee ground used as alternative adsorbents for Cr(VI) removal. Batch experiments indicate complete adsorption of $10–30 \, mg \, L^{-1}$ Cr(VI) from synthetic wastewater at pH 2.0 for 180 min, 30 °C and 250 rpm with $2 \, g \, L^{-1}$ of adsorbent dose used. SEM and TEM images together with EDS results revealed that the nature of the adsorbents was altered after Cr(VI) adsorption and noticeable chromium accumulation was found on the adsorbent surfaces. A change in carbon and oxygen functional groups on the surface of the adsorbent was observed from FTIR and XPS analyses after Cr(VI) adsorption. Freundlich sorption isotherm model correlated best with the Cr(VI) adsorption equilibrium data for the $10–250 \, mg \, L^{-1}$ concentration range, for both adsorbents. The rate of Cr(VI) adsorption on both adsorbents was found to fit better with pseudo-second-order kinetic model. Maximum adsorption capacity of $94.34 \, mg \, g^{-1}$ for mixed waste tea and $87.72 \, mg \, g^{-1}$ for coffee ground was estimated. Reusability studies recommended both

adsorbents can be reused four times with the remaining adsorption efficiency >50%. Study on a 100 L of packed-bed reactor showed the breakthrough time of adsorption for mixed waste tea as 30 min in $100 \, mg \, L^{-1}$ Cr(VI) concentration.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.01.100.

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