One-Step and Nondestructive Reduction of Cr(VI) in Pork by High-Energy Electron Beam Irradiation

Jingya Ren, Guilong Zhang, Dongfang Wang, Jie Han, Zhengyan Wu, and Dongqing Cai

Abstract: Because of the wide use of chromium-containing feed, much hexavalent chromium (Cr(VI)) tends to accumulate in pork. In order to decrease the toxicity of Cr(VI)-containing pork for human beings, high-energy electron beam (HEEB) irradiation was used to reduce highly toxic Cr(VI) to low toxic trivalent chromium (Cr(III)) in lean, fat, and marbled pork. HEEB irradiation could efficiently and nondestructively reduce both free and adsorbed Cr(VI) in pork, achieving the highest reductive efficiency (RE) of 98.03%. Therein, hydrated electrons (e_{aq}^-) and hydrogen radical (•H) generated during the irradiation process probably played key roles in the reduction. The effects of irradiation dose, initial concentration of Cr(VI), pH, temperature, salinity, and oil on the RE were investigated to obtain the optimal reduction conditions, proving the high universality of this approach. This work provides a clean and low-cost method for removing Cr(VI) from pork, which is important to ensure food safety.

Keywords: Cr(VI)-containing pork, hexavalent chromium, high energy electron beam, reductive efficiency

Practical Application: This work describes a facile, nondestructive, and clean method for removing Cr(VI) from meat product, which may have a potential application prospect in ensuring food quality and safety.

Introduction

Heavy metal ions tended to access human body through food chain resulting in severe threatening for the health (Gámiz et al., 2017; Yang, Wang, Chen, Li, and Peng, 2017; Nookabkaew, Rangkadilok, Prachoom, & Satayavivad, 2016), therefore heavy metal ions remediation has become one of the hottest topics in environment and agriculture fields nowadays. Currently, in order to reduce the incidence of livestock and promote the growth of pigs (Choi et al., 1998), plenty of heavy metal ions were added to feeds, such as Cr^{3+}, Cu^{2+}, Zn^{2+}, and so on (Huang et al., 2017; Xu, Su, Liu, Li, & Bian, 2010). Therein, owing to the wide use of chromium-containing feed for pigs, a part of trivalent chromium (Cr(III)) in pigs was easily to be transformed to hexavalent chromium (Cr(VI)) through oxidation reaction in vivo, and the resulting Cr(VI) tended to accumulate in pork. After the uptake of Cr(VI)-containing pork by human beings, Cr(VI) was easily to accumulate in the body and displayed high toxicity and potential carcinogenicity, resulting in cardiovascular and cerebrovascular diseases, liver damage, pulmonary congestion, severe diarrhea and so on (Lendinez, Lorenzo, Cabrera, & Lopez, 2001; Vacchina, de la Calle, & Seby, 2015). Therefore, it is rather imperative to develop an approach to eliminate Cr(VI) in pork.

In the past decades, a variety of approaches have been developed for Cr(VI) removal including physical (electrical enrichment and washing), chemical (reduction, adsorption, and inactivation), and biological (plant enrichment) methods (Costa, & Morel, 1993; Li, Yu, & Neretnieks, 1998; Zhang et al., 2013). These methods were primarily suitable for Cr(VI) removal in water and soil but pork because they could damage pork in different degrees and thus decrease the commercial quality of pork. Additionally, most of these methods exhibited complex procedures and long periods. Therefore, it is urgent to develop a one-step and nondestructive method for removing Cr(VI) in pork. In our previous work, it was found that high-energy electron beam (HEEB) irradiation could immediately and effectively reduce highly toxic Cr(VI) in water and soil to low toxic Cr(III) without any destruction on water and soil (He et al., 2015; Wang et al., 2017; Wang et al., 2017; Zhang, Zhang, Cai, & Wu, 2015). In addition, HEEB irradiation possessed other advantages of high penetration depth (approximately 50 cm in water), low cost (200 dollars per ton), and without any additives (Wang, Zhang, Qiu, Cai, & Wu, 2016; Xiang, Wang, Song, Cai, & Wu, 2013). Hence, HEEB irradiation can potentially be used as an ideal method to remove Cr(VI) in pork through reduction.

In this work, the reductive efficiency of HEEB irradiation on Cr(VI) in lean, fat, and marbled pork was investigated. The result indicated that HEEB irradiation could efficiently reduce free and adsorbed Cr(VI) in pork, achieving a reductive efficiency of approximately 80% for the free Cr(VI). Meanwhile, the effect of pH, temperature, salinity, and oil on the reductive efficiency of free Cr(VI) was investigated to obtain the optimal condition. Importantly, HEEB irradiation could effectively transform the adsorbed Cr(VI) ions to free ones through desorption and then reduce them to Cr(III). Therefore, this work provides a facile, nondestructive, and clean method for removing Cr(VI) from meat product, which may have a potential application prospect in enhancement of food safety.

Materials and Methods

Materials

$K_2Cr_2O_7$ and other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Company (Shanghai,

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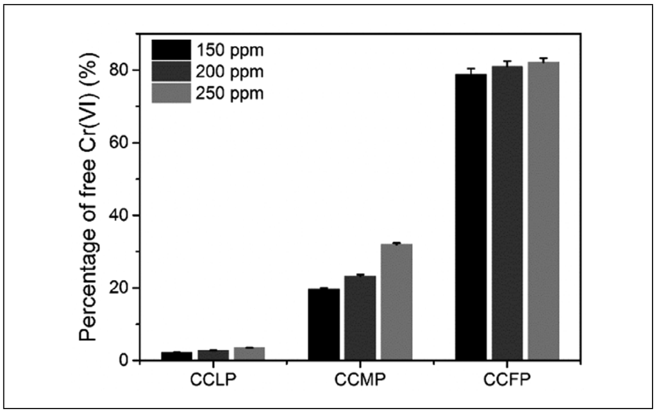

Figure 1–Percentage of free Cr(VI) in total Cr(VI) with different initial concentrations in CCLP, CCMP, and CCFP.

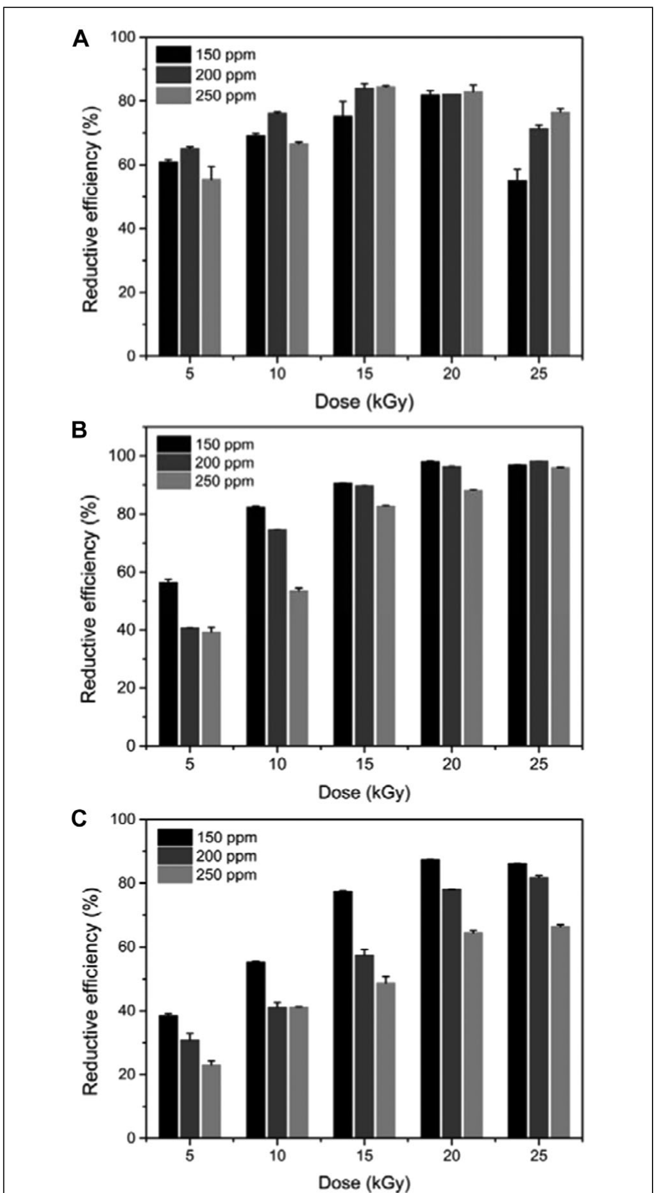

Figure 2–Reduction performance of HEEB irradiation on free Cr(VI) with different initial concentrations of total Cr(VI) in (A) CCLP, (B) CCMP, and (C) CCFP.

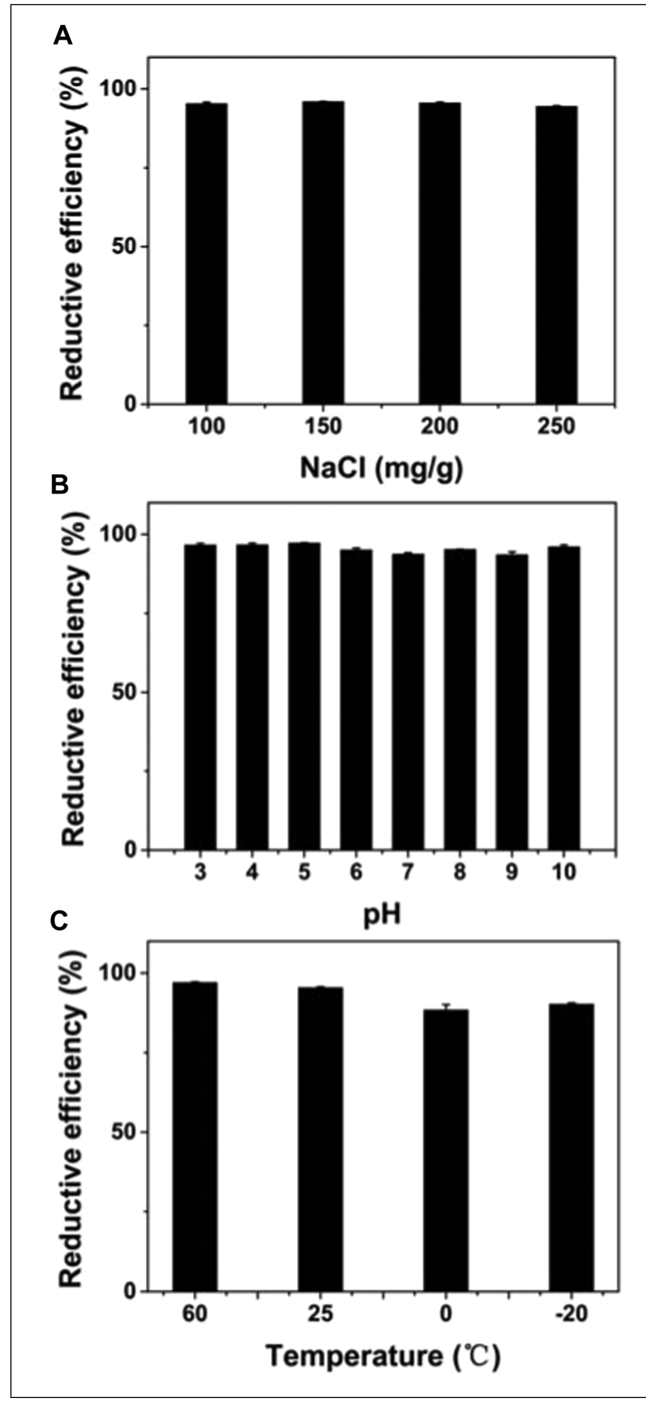

Figure 3–Effect of (A) salinity (30 °C, pH 4.5), (B) pH (30 °C), and (C) temperature (pH 4.5) on RE of HEEB irradiation (dose of 20 kGy) on free Cr(VI) (total Cr(VI) initial concentration of 150 ppm) in CCLP.

China). Pork was purchased from a market in Dongpu Island (Hefei, China). Deionized water was used throughout this work.

Preparation and HEEB irradiation treatment of Cr(VI)-containing pork (CCP)

Lean, fat, and marbled pork were cut into small pieces (0.5 cm × 0.5 cm × 0.5 cm) respectively and the resulting samples were boiled in water for 5 min. Then, 1 mL of Cr(VI) solution (300, 400, or 500 mg/L) was evenly added to these three kinds of pork (2 g) to obtain Cr(VI)-containing lean pork (CCLP),

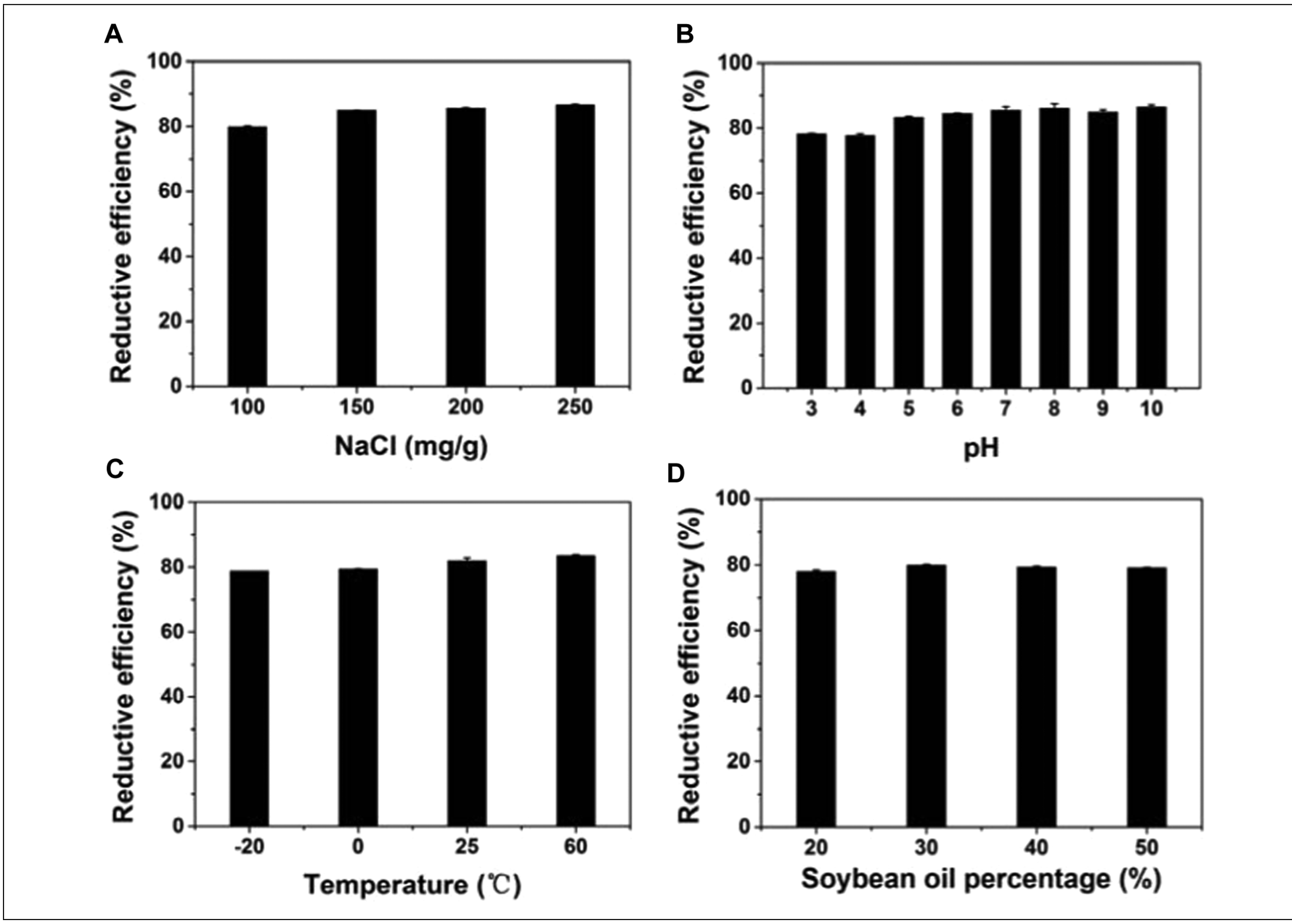

Figure 4–Effect of (A) salinity (30 °C, pH 4.5), (B) pH (30 °C), (C) temperature (pH 4.5) and (D) soybean oil (30 °C, pH 4.5) on RE of HEEB irradiation (dose of 20 kGy) on free Cr(VI) (initial concentration of 86 ppm) in RCCLP.

Cr(VI)-containing fat pork (CCFP), and Cr(VI)-containing marbled pork (CCMP). Afterward, these CCP samples in a sealed plastic centrifuge tube (50 mL) were irradiated by a HEEB accelerator (10 MeV and 10 kW) (IHI10, IHI Co., Japan) with doses of 5, 10, 15, 20, and 25 kGy. The irradiated sample was added to deionized water (24 mL) respectively and the resulting system was shaken for 30 min to extract free Cr(VI) from CCP to water. The concentration of free Cr(VI) in the supernatant of the resulting solution was determined after centrifugation (12000 rpm) for 6 min through diphenylcarbazine method (Ke, Huang, Zhang, & Yu, 2011). All experiments were performed in triplicate. The reductive efficiency (RE) of free Cr(VI) in CCP was calculated according to equation (1):

$$\mathrm{RE}\,(\%) = (C_0 - C_t)/C_0 \times 100\% \qquad (1)$$

where C_0 (mg/L) and C_t (mg/L) are the concentrations of free Cr(VI) before and after HEEB irradiation respectively.

The percentage of free Cr(VI) in total Cr(VI) before HEEB irradiation could be calculated according to Eq. (2):

$$\mathrm{Percentage}\,(\%) = C_0/C_{\mathrm{total}} \times 100\% \qquad (2)$$

where C_0 (mg/L) and C_{total} (mg/L) are the concentrations of free and total Cr(VI) in CCP before HEEB irradiation.

Effect of pH, temperature, and salinity on Cr(VI) reduction

CCLP (2 g) with initial Cr(VI) concentration of 150 ppm was placed in sealed centrifuge tubes respectively which were then irradiated by HEEB with a dose of 20 kGy at different temperatures (–20, 0, 25, and 60 °C) under various pH conditions (3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0) and diverse salt levels (0.2, 0.3, 0.4, and 0.5 g). Then the resulting Cr(VI) concentrations in those samples were determined to calculate the RE according to equation (1). Besides, the influences of NaCl, pH, temperature, and soybean oil (contents of 20%, 30%, 40%, and 50%) on the reduction performance of HEEB (20 kGy) for free Cr(VI) (86 ppm) in 2 g of real Cr(VI)-containing lean pork (RCCLP) have been investigated under the same conditions.

Characterization

The morphology and microstructure of lean pork were observed on a scanning electron microscope (SEM) (Sirion 200, FEI Co., U.S.A.), wherein the lean pork sample was dried in a vacuum freeze-dryer (–80 °C) for 48 hr and then cut into small pieces (0.5 mm × 0.5 mm × 0.1 mm). The valence of Cr was measured by an X-ray photoelectron spectroscope (XPS) (ESCALAB 250, Thermo-VG Scientific Co., U.S.A.) in vacuum with total acquisition time of 51.1 s, spot size of 500 μm, pass energy of 30.0 eV, and energy step size of 0.05 eV. In order to prepare the XPS sample, CCLP (2 g) with initial Cr(VI) concentration of 150 ppm was dried in a vacuum freeze-dryer (–80 °C) for 48 hr and then

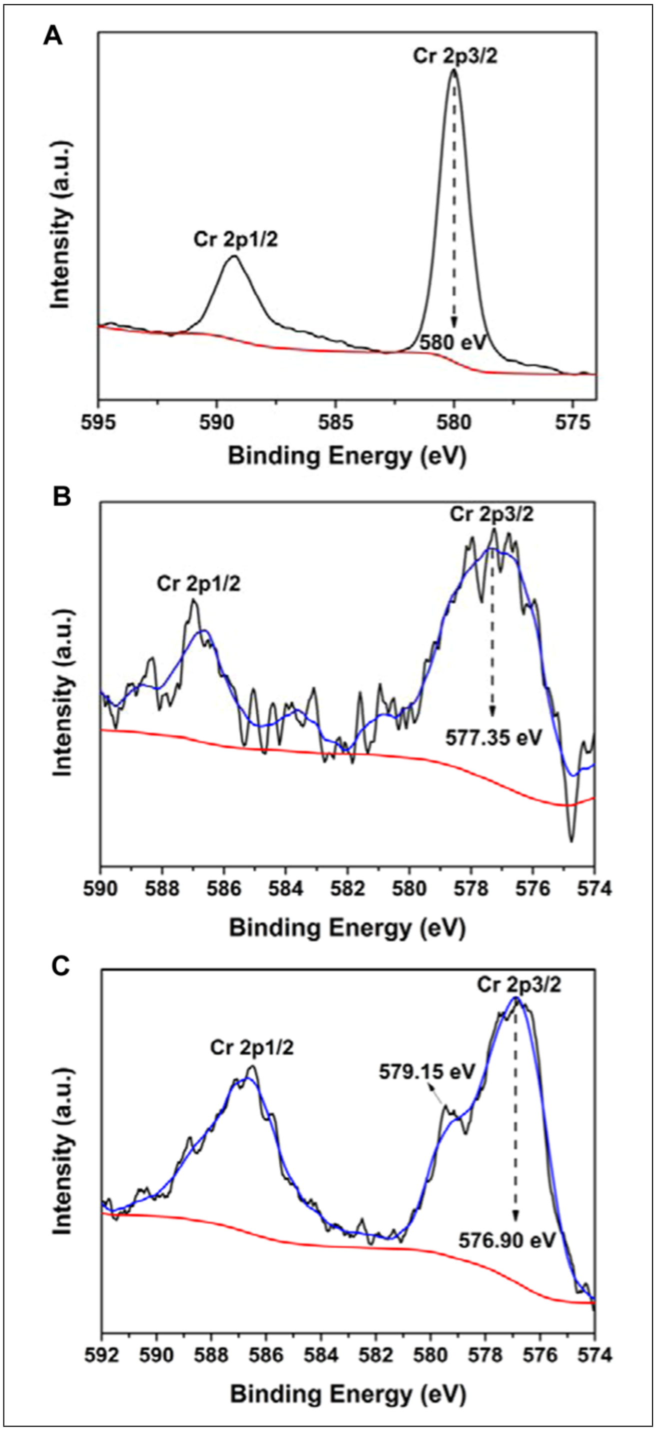

Figure 5–(A) Cr2p XPS spectrum of K_2CrO_7; (B and C) Cr2p XPS spectra of CCLP before and after HEEB irradiation with dose of 20 kGy at 25 °C.

ground to powder (100 to 200 mesh). The concentration of free Cr(VI) was measured using an ultraviolet-visible (UV-vis) spectrophotometer (UV Lambda 365, PerkinElmer Co., U.S.A.) at a wavelength of 540 nm (Ke et al., 2011).

Results and Discussion

Free Cr(VI) ratio in CCLP, CCMP, and CCFP

Generally, Cr(VI) in pork displayed two dominant forms of free and adsorbed because a part of Cr(VI) could be adsorbed mainly by protein (Lundin et al., 2012). The ratio of free Cr(VI) ions in total Cr(VI) was investigated in CCLP, CCMP, and CCFP to obtain the adsorption performance of these three typical kinds of pork. It could be seen in Figure 1 that the percentage of free Cr(VI) in CCP displayed an order (high to low) of CCFP (80% to 85%), CCMP (20% to 35%), and CCLP (2% to 4%). It was worth noting that the protein content in these three kinds of pork exhibited the opposite order as the percentage of free Cr(VI), indicating that the amount of free Cr(VI) decreased with the increasing protein amount. This was probably because protein possessed plenty of active groups such as $-NH_2$ which possessed positive charges under neutral and acid conditions and thus could adsorb negatively charged Cr(VI) ions via electrostatic attraction. Therefore, higher protein content resulted in higher adsorbed Cr(VI) amount and thus lower free Cr(VI) amount. Noteworthily, the dominant component of fat was triacylglycerol (CH_2COOR_1-$CHCOOR_2$-CH_2COOR_3) which tended to transform to glycerinum and aliphatic acid through hydrolysis, wherein the glycerinum possessed no charge and aliphatic acid possessed negative charges under neutral and acid conditions, thus fat was difficult to adsorb negatively charged Cr(VI) ions. In addition, with the increase of initial Cr(VI) concentration, the percentages of free Cr(VI) in CCLP, CCMP, and CCFP increased in different degrees, owing to the decreasing relative amount of adsorption sites.

Reduction performance on free Cr(VI)

The reduction performance of HEEB irradiation on free Cr(VI) in CCLP, CCMP, and CCFP was investigated. As shown in Figure 2, HEEB irradiation could significantly reduce the free Cr(VI) in these three kinds of pork, wherein, briefly, the RE of Cr(VI) increased with the irradiation dose initially (5 to 20 kGy), and then (20 to 25 kGy) decreased, reaching the maximum value at 20 kGy. It was proposed that hydrated electrons (e_{aq}^-) and hydrogen radical (•H) generated during the HEEB irradiation process might play key roles in the reduction of free Cr(VI) (Cooper, Nickelsen, Green, & Mezyk, 2002). Generally, the amounts of e_{aq}^- and •H increased with the HEEB dose, so that more Cr(VI) ions were reduced to Cr(III). When the amount of free Cr(III) was higher than a certain degree, it might inhibit the contact of reductive particles (e_{aq}^- and •H) with Cr(VI) because of the indissolubility of Cr(III), thereby resulting in decrease of RE at dose higher than 20 kGy.

In addition, Figure 2B and C demonstrated that, at a certain dose, the RE of free Cr(VI) in both CCMP and CCFP decreased to different extents with the increase of initial total Cr(VI) concentration, because the number of reductive particles for each free Cr(VI) ion decreased. Particularly, as shown in Figure 2A, the RE of free Cr(VI) in CCLP displayed an increase-decrease trend with the initial concentration of total Cr(VI) at doses of 5 and 10 kGy, while an increase trend at doses higher than 10 kGy. Notably, the RE of free Cr(VI) in CCLP and CCMP were almost the same, while that in CCFP was significantly lower compared with CCLP and CCMP, attributing to the dramatically higher free Cr(VI) amount in CCFP (Figure 1). Based on the preceding analyses, HEEB possessed a high reduction ability on free Cr(VI) in lean, marbled, and fat pork.

Effect of salinity, pH, and temperature on Cr(VI) reduction

In general, cooked meat products possessed a variety of salinity and pH originated from the addition of condiments such as salt, vinegar and so on. Besides, the cooked meat products were commonly stored under temperatures from −20 to 60 °C. As such, the

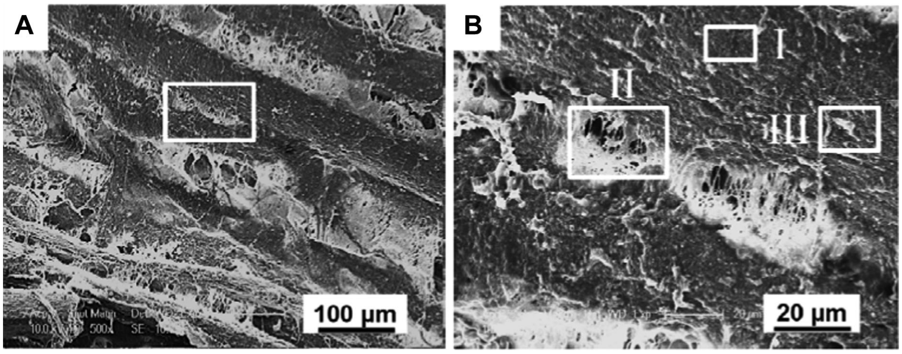

Figure 6–(a) SEM image of the lean pork surface; (b) Magnified image of the rectangle region in (a). Rectangles I-III: muscle fibers, connective tissue, and adipose tissue, respectively.

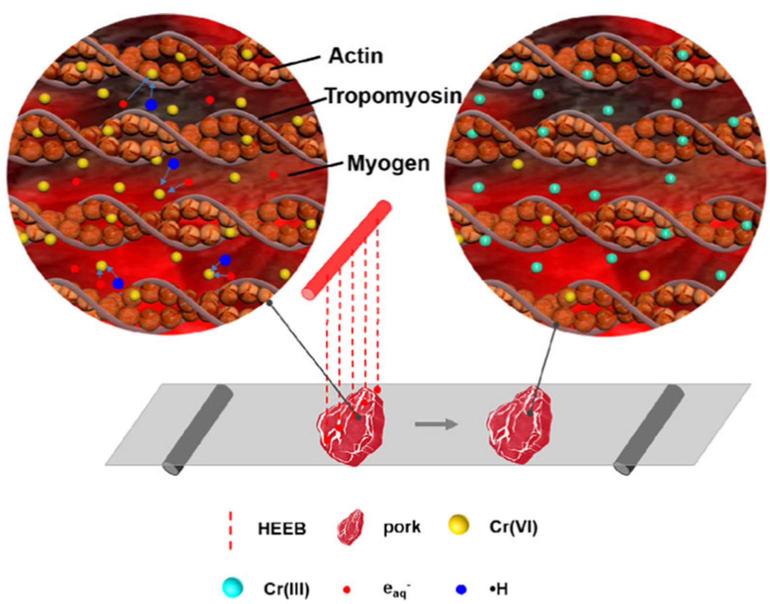

Figure 7–Schematic diagram of the reduction mechanism of HEEB irradiation on Cr(VI) in CCMP.

influence of salinity, pH, and temperature on the RE of HEEB irradiation on free Cr(VI) in CCLP was investigated to obtain the universality of this technology. As displayed in Figure 3A and B, there was no significant difference in the RE of free Cr(VI) in CCLP with different salinity and pH, indicating that salinity and pH had little influence on the reduction performance of HEEB. This result also proved that the activities of e_{aq}^- and •H were not obviously affected by salinity in range of 100 to 250 mg/g and pH in range of 3 to 10.

Additionally, the effect of temperature (–20, 0, 25, and 60 °C) on the reduction performance of HEEB irradiation for free Cr(VI) in pork was investigated. As shown in Figure 3C, with the increase of temperature, the RE exhibited a general slight increase trend especially when the temperature increased from 0 to 25 °C, which was probably related to the increasing activities of e_{aq}^- and •H and their contact probabilities with free Cr(VI). These results suggested that salinity, pH, and temperature showed little influence on the RE of HEEB irradiation on free Cr(VI) in CCLP. In other words, HEEB irradiation displayed a high universality and stability.

Besides, the influences of NaCl, pH, temperature, and soybean oil (contents of 20%, 30%, 40%, and 50%) on the reduction performance of HEEB (20 kGy) for Cr(VI) (86 ppm) in RCCLP have been also investigated. As shown in Figure 4A to C, RE of HEEB irradiation on free Cr(VI) in RCCLP were almost the same under different NaCl concentrations, pH, and temperature, which was consistent with the result from CCLP. Additionally, soybean oil content also did not show any significant impact on the RE of free Cr(VI) in RCCLP (Figure 4D). Those results indicated that this technology could be also used in real samples and displayed a high stability against NaCl, pH, temperature, and soybean oil.

Effect of HEEB irradiation on Cr(VI) chemical states in CCLP

Besides, XPS analyses were carried out in order to obtain the chemical states of Cr(VI) in CCLP before and after HEEB irradiation. As displayed in Figure 5A, the characteristic peak of Cr(VI) at 580 eV was found in the Cr2p3/2 XPS spectrum of K_2CrO_7. Compared with K_2CrO_7, the characteristic peak of Cr(VI) in CCLP shifted to 577.35 eV (Figure 5B), probably because a part of Cr(VI) ions were adsorbed by the protein in lean pork through electrostatics attraction. Interestingly, after HEEB irradiation, the characteristic peak of adsorbed Cr(VI) at 577.35 eV disappeared, while a shoulder peak at 579.15 eV ascribed to free Cr(VI) and a peak at 576.9 eV (Figure 5B) corresponding to Cr(III) appeared (Cooper et al., 2002; Halada & Clayton, 1991; Qiu et al., 2014), suggesting that adsorbed Cr(VI) ions were probably transformed to free Cr(VI) through the desorption of HEEB irradiation, and then most of the free Cr(VI) was reduced to Cr(III). In a word, the XPS analyses illustrated that HEEB irradiation could effectively transform adsorbed Cr(VI) ions in CCLP to free Cr(VI) a part of which were then reduced to Cr(III).

Mechanism study

Pork consisted of muscle fibers (rectangle I), connective tissue (rectangle II), and adipose tissue (rectangle III) (Figure 6A). Therein, the muscle fibers, made of several kinds of proteins including actin, tropomyosin, myogen, and myofibrillar, possessed plenty of positive charges because of the existence of abundant $–NH_3^+$ and thus could adsorb Cr(VI) ions via electrostatic attraction (Lundin et al., 2012). The connective tissue displayed a network structure (Figure 6B), which helped Cr(VI) ions access the muscle fibers and thus promoted the adsorption of Cr(VI). Meanwhile, other Cr(VI) ions which were not adsorbed mainly distributed in adipose tissues. Based on the preceding analyses, during the HEEB irradiation process, a large quantity of reductive particles including e_{aq}^- and •H generated because of H_2O radiolysis and could effectively reduce free Cr(VI) to Cr(III). At the same time, HEEB irradiation could transform the adsorbed Cr(VI) to free Cr(VI) which was then reduced to Cr(III). The mechanism on the reduction of HEEB irradiation for Cr(VI) in pork was demonstrated in the schematic diagram (Figure 7).

Conclusion

The reduction performance of HEEB irradiation for Cr(VI) in pork was investigated, the results indicated that HEEB could immediately and effectively reduce free Cr(VI) to Cr(III) without any damage to pork. Importantly, HEEB irradiation could transform the adsorbed Cr(VI) to free Cr(VI) which was then reduced to Cr(III). Reductive particles (e_{aq}^- and •H) generated during the irradiation process were proposed to be the dominant reason for the reduction. Additionally, this method displayed a high stability against temperature, pH, salinity, and soybean oil. Therefore, this work provided a one-step, nondestructive, and clean technology to remove Cr(VI) in pork, which might have a high application value.

Acknowledgments

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Author Contributions

The experiments of this work were carried out by Jingya Ren, Guilong Zhang, and Dongfang Wang under the supervision of Zhengyan Wu and Dongqing Cai. The paper was written by Jingya Ren and revised by Zhengyan Wu and Dongqing Cai. Jie Han helped to edit the figures.

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