



ELSEVIER

Contents lists available at [ScienceDirect](http://www.sciencedirect.com)

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

IChemE ADVANCING CHEMICAL ENGINEERING WORLDWIDE



Reassessment of adsorption–reduction mechanism of hexavalent chromium in attaining practicable mechanistic kinetic model

Zhung-Gia Ng^a, Jun-Wei Lim^{b,*}, Hanita Daud^b, Si-Ling Ng^a,
Mohammed J.K. Bashir^c

^a School of Chemical Sciences, Universiti Sains Malaysia, 11800 Gelugor, Penang, Malaysia

^b Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak Darul Ridzuan, Malaysia

^c Department of Environmental Engineering, Faculty of Engineering and Green Technology (FEGT), University Tunku Abdul Rahman, 31900 Kampar, Perak, Malaysia

ARTICLE INFO

Article history:

Received 16 September 2015

Received in revised form 18 January 2016

Accepted 27 February 2016

Available online 4 March 2016

Keywords:

Hexavalent chromium

Adsorption

Reduction

Mechanism

Kinetic

Modeling

ABSTRACT

The insufficiency of mechanistic kinetic model which incorporated the adsorption–coupled reduction mechanism of Cr(VI) was identified and subsequently, reinforced mechanism which better describe the adsorption–reduction of Cr(VI) by sawdust sorbent is proposed. The H⁺ ion term which was presumably constant in the previous mechanism is currently incorporated into the proposed mechanism, showing the reduction of 2 mol of Cr(VI) require 1 mol of H⁺ ion. As such, the poorer fit of former kinetic model at increasing initial Cr(VI) concentration and solution pH and decreasing dosage of sawdust was justified. The proposed mechanism is admissible when the H⁺ concentration is greater than the Cr(VI) concentration at all the arbitrary time of measurement. In the case of reverse condition, the proposed mechanism could no longer describe the Cr(VI) adsorption–reduction process adequately since the surface of sorbent is not fully protonated. The kinetic model derived from the proposed mechanism suggests that the kinetics of Cr(VI) adsorption–reduction is first-order with respect to Cr(VI), organic contents participating in Cr(VI) reduction and H⁺. Later, the inhibition coefficient derived from the new kinetic model permits the quantification of inhibition effect of various metals acting on the rate of Cr(VI) removal, giving rise to more factual understanding in real application.

© 2016 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Biosorption is a process of sequestering metals, metalloids, compounds and particulates from the solution using biological materials. As such, countless biological waste materials has been employed for various purposes of biosorption studies (Namasivayam and Sureshkumar, 2007; Wang et al., 2008; Sharma et al., 2013; de Sousa et al., 2014; Nakhli et al., 2014; Halet et al., 2015; Qi et al., 2015; Shehzad

et al., 2015). Throughout the extensive studies performed by researchers, the mechanisms of biosorption have been found to involve ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation, reduction and microprecipitation. There is also a possibility for redox reaction to take part in biosorption as well. The combination of these processes may also occur in any case of biosorption (Kratochvil and Volesky, 1998; Dönmez et al., 1999; Volesky, 2001; Sud et al., 2008; Wang and Chen, 2009; Batista et al., 2011;

* Corresponding author. Tel.: +60 53687664; fax: +60 53655905.

E-mail address: junwei.lim@petronas.com.my (J.-W. Lim).

<http://dx.doi.org/10.1016/j.psep.2016.02.014>

0957-5820/© 2016 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Silva et al., 2012). However, the understanding of the mechanism is still not comprehensive and inconclusive particularly in the case of hexavalent chromium or simply Cr(VI). Among all heavy metals that have been studied for biosorption, Cr exhibits a distinctly different behavior. The characteristics of having two stable ions, cation for Cr(III) and oxyanion for Cr(VI), in water, which was overlooked by numerous of researchers in earlier studies, resulted in four proposed mechanisms to describe the behavior of Cr(VI) removal by sorbent.

Anionic adsorption is the typical mechanism generally accepted by a pool of researchers (Raji and Anirudhan, 1998; Basha and Murthy, 2007; Hamed Mosavian et al., 2012; Li et al., 2015; Rangabhashiyam and Selvaraju, 2015). A traditional procedure of Cr analysis was typically used by the researchers who agreed to this mechanism in which either only residual Cr(VI) or total Cr in the solution was analyzed. As such, these researchers failed to identify the presence of Cr(III) in the solution and perceived that the adsorption of Cr(VI) onto and into the sorbents was merely due to the electrostatic attraction between the negatively charged Cr(VI) and the positively charged sorbents. This incomprehensive interpretation led them to conclude that anionic adsorption played the role in the removal of Cr(VI) via adsorption.

In the anionic and cationic adsorption mechanism, Daneshvar et al. (2002) predicted that at low pH, H^+ ions would combine with negatively charged organic functional groups on the surface of sorbents, leading to the enhancement of sorption between anionic Cr(VI) species and protonated functional groups. These researchers also claimed that the reduced form of Cr(VI) species, i.e., Cr(III) ions, were chelated in the solution, minimizing the repulsion between the cationic Cr(III) ions and the positively charged functional groups on the surface, $R-NH_3^+$, for instance. Accordingly, both Cr(III) and Cr(VI) species were adsorbed onto sorbents in their study which was later supported by Hasan et al. (2008). From the research, they saw their exploited sorbent turned greenish after the adsorption process and inferred the instance was due to the amassment of Cr(III) ions on the surface of sorbent, judging from the fact that Cr(III) species is commonly known with color of green. Apparently, these two groups of researchers pointed out that the adsorption of Cr(VI) involved anionic and cationic adsorption, which occurred simultaneously.

On another note, Cabatingan et al. (2001) anticipated that Cr(VI) sorption involved the process of simultaneous adsorption and reduction of chromate, supporting the reduction and anionic adsorption mechanism. However, the researchers found Cr(III) ions desorbed from the sorbents instead of Cr(VI) species, which was conflicting with their expectation. Indeed, they stressed this phenomenon to the difficulty in maintaining Cr(VI) oxidation state during the desorption process. This was an indiscriminate account since they failed to recognize that it could be the Cr(III) ions, rather than Cr(VI), bound to their sorbents and that were partially desorbed in the interim. Likewise, Aoyama (2003) proposed that the adsorption of Cr(VI) involved two independent pathways, namely the reduction of Cr(VI) to Cr(III) and the sorption of Cr(VI) by sorbents. This researcher contended that Cr(III) was in its bulky form, i.e., $[Cr(H_2O)_6]^{3+}$, which severely hindered its sorption to the active sites of sorbents. In the light of these reported cases to support the reduction and anionic adsorption mechanism, the conclusion of Cr(VI) adsorption was a process of combining the Cr(VI) reduction in which Cr(III) ions remained in the solution and the Cr(VI) sorption was insistently asserted.

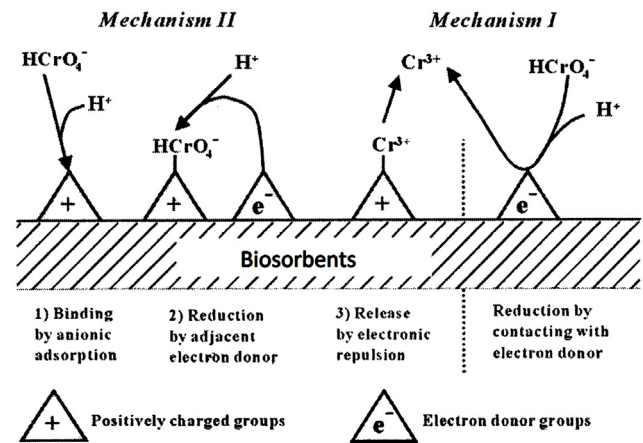


Fig. 1 – Direct reduction (Mechanism I) and indirect reduction (Mechanism II) (Park et al., 2005).

The last one is adsorption–coupled reduction mechanism which was evidenced by the investigation of Cr sorption onto lignocellulosic substrate reported by Dupont and Guillon (2003). The Cr(III) species in their study was found to adsorb onto the sorbent via X-ray photoelectron spectroscopy analysis. Later, Park et al. (2007a) examined the Cr species in sixteen sorbents using similar analysis method and also found Cr(III) ions were adsorbed onto all the sorbents, which was of great contrast with the mechanisms described earlier. According to adsorption–coupled reduction mechanism as proposed by these researchers, the Cr(VI) species was initially reduced before being adsorbed by the sorbents in the form of Cr(III) ions. From this proposed mechanism, there were two reduction possibilities, namely via direct reduction and indirect reduction mechanisms (Fig. 1). In the direct reduction mechanism, the Cr(VI) species together with H^+ ions came in contact with the electron donor groups on the surface of sorbent and subsequently reduced. A fraction of generated Cr(III) ions were released into the solution while the remains would be bound by the positively charged groups. For the indirect reduction mechanism case, the Cr(VI) species was initially bound by the positively charged groups on sorbent surface and then reduced by the adjacent electron donor groups. The generated Cr(III) ions were either bound to sorbents via complexation or released into the solution due to repulsion with the positively charged groups.

With exception applied to the anionic adsorption mechanism, the presence of Cr(III) ions were predicted by the other three mechanisms: (a) anionic and cationic adsorption mechanism, (b) reduction and anionic adsorption mechanism and (c) adsorption–coupled reduction mechanism; sharing a common idea, i.e., Cr(VI) species were reduced by the sorbents. However, the distinct characteristic in each of them was the mechanism of anionic and cationic adsorption suggested that both Cr(III) and Cr(VI) species were adsorbed by the sorbents, the mechanism of reduction and anionic adsorption outlined that only Cr(VI) species was adsorbed whereas Cr(III) ions were released into the solution due to the repulsion force and lastly, the mechanism of adsorption–coupled reduction accentuated that only Cr(III) ions were adsorbed by the sorbents.

Literature search revealed that there were generally two types of kinetic models applied to describe the removal of Cr(VI) by sorbents, namely the empirical and mechanistic types. The typical empirical type of model used was pseudo-second-order adsorption model which was frequently exploited by the researchers (Baral et al., 2006; Wu et al.,

Download English Version:

<https://daneshyari.com/en/article/588064>

Download Persian Version:

<https://daneshyari.com/article/588064>

[Daneshyari.com](https://daneshyari.com)