



# Chromium(VI) adsorption onto boehmite nanoparticles obtained by cost effective “green” synthesis

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## Abstract

Mesoporous boehmite nanopowder was prepared by a simple route and used as an efficient adsorbent for chromium(VI) removal. Chromium(VI) is considered to be potentially carcinogenic to humans, thus, removal of Cr(VI) ions from aqueous solution is of great importance. Batch adsorption experiments were conducted to study the effects of contact time and initial concentration of Cr(VI). The boehmite prepared by neutralization of sodium aluminate solution from Bayer liquor and glucose as nonionic surfactant is environmentally friendly material for potential industrial scale production. It has the high specific surface area (296 m<sup>2</sup>/g) and high adsorption capacity (32.92 mg/g after 72 h) for the removal of Cr(VI) from aqueous solutions. This high removal percentage is in an excellent agreement with the capacity calculated by the pseudo-second order model (33.11 mg/g). The equilibrium isotherm data fitted well with the Langmuir model ( $R^2=0.996$ ), suggesting a uniform surface nature of the prepared nanoparticles.

**Keywords** Boehmite · Mesoporous · Adsorption · Chromium · Langmuir

## Introduction

Water is an essential part of the everyday life of humans. It is used extensively in people's homes, industry, agriculture, etc. These days a great concern is devoted to water consumption and remediation of polluted water from industry and households. Even though it makes about two thirds of the Earth's surface, the amount of usable water is only about

0.3% (Bhattacharya et al. 2018). This is why there is an extensive effort to purify water in order to reuse it. Water often contains suspended colloids, bacteria, viruses, organic and inorganic pollutants that need to be removed. Nanopowders of various metal oxides could be one of the possible solutions for wastewater treatment due to their high specific surface area, adsorption capacity and chemical reactivity (Afkhami et al. 2010; He et al. 2019; Nagpal and Kakkar 2019).

Nanopowders based on aluminum oxide and hydroxide are well-known group of materials and they are usually referred to as alumina. Two of the most important types of alumina adsorbents are boehmite and  $\gamma$ -alumina. Boehmite is aluminum oxyhydroxide (AlOOH) which transforms into  $\gamma$ -alumina when heated above 400 °C (Hicks and Pinnavaia 2003). Due to the importance of boehmite, but also  $\gamma$ -alumina, in the heterogeneous catalysis, composite materials, adsorption, membranes, bioceramics, batteries, etc., (Hicks and Pinnavaia 2003; Kiss and Boskovic 2012; Kocjan et al. 2017; Laachachi et al. 2009; Luo et al. 2016; Majhi et al. 2009; Roy et al. 2018; Said et al. 2019; Solovev et al. 2019) boehmite is produced industrially at a very large scale and it is predicted that the global market of boehmite will reach 507.7 million \$ until year 2027 (MarketWatch LLC, n.d.). There are several different methods to prepare

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pure boehmite usually by some modification of hydrothermal method (Cai et al. 2010, 2009; Filho et al. 2016; Ge et al. 2013; Ren et al. 2004; Zhang et al. 2009) or by using sol–gel synthesis and various surface modifications (Cai et al. 2014; Hicks and Pinnavaia 2003; Park et al. 2007; Said et al. 2019; Wang et al. 2013). However, hydrothermal method is time and energy consuming and sol–gel process involves expensive metal–organic precursors and chemicals which are usually environmentally hazardous. Milanovic et al. (Milanović et al. 2018) reported recently that pure boehmite nanopowder could be obtained at room temperature by using neutralization of sodium aluminate solution from Bayer liquor and glucose as nonionic surfactant. This process is both energy efficient and environmentally friendly. It gives boehmite nanocrystalline powder of high purity and high specific surface area.

Boehmite is unique since it is the only precursor for  $\gamma$ ,  $\delta$  and  $\theta$ -alumina phases upon heating and before transforming to  $\alpha$ -alumina (Hicks and Pinnavaia 2003; Santos et al. 2000). Phase transformations of boehmite from 400 to 1000 °C are a consequence of thermal dehydroxilation. They are usually topotactic transitions which preserve microstructural and textural features such as specific surface area, pore shape and diameter (Hicks and Pinnavaia 2003; Milanović et al. 2018; Santos et al. 2000). Since boehmite ( $\text{AlOOH}$ ) has more surface –OH groups than  $\gamma$ -alumina ( $\text{Al}_2\text{O}_3$ ), the adsorbing properties and selectivity can be tuned by processing and temperature treatment. This is why there are plenty of literature reports about the adsorption characteristics of boehmite and/or  $\gamma$ -alumina for wide range of both organic and inorganic species: Congo red (Cai et al. 2010; Nagpal and Kakkar 2019; Wang et al. 2013), phenol (Cai et al. 2009), phosphate (Hano et al. 1997; Tanada et al. 2003), arsenic (Dubey et al. 2017; Ogata et al. 2006), cadmium (Granados-Correa et al. 2011; Hota et al. 2008; Sun et al. 2019), chromium (Cai et al. 2014; Ge et al. 2013; Luo et al. 2016) and various other ions (Afkhami et al. 2010; Majhi et al. 2009; Yan et al. 2017).

Chromium is one of the most dangerous pollutants in wastewaters. It exists in several oxidation states, but the most common species are the chromium(VI) and chromium(III). Chromium(VI) is highly toxic and carcinogenic. Therefore, a great effort has been undertaken to remove it from water (Granados-Correa and Jiménez-Becerril 2009; Johnston and Chrysochoou 2015). There are several reports that alumina nanopowders, mostly pure or modified boehmite and  $\gamma$ -alumina, could be considered as suitable for chromium adsorption and its removal from water (Afkhami et al. 2010; Cai et al. 2014; Granados-Correa and Jiménez-Becerril 2009; Johnston and Chrysochoou 2015; Luo et al. 2016; Zhang et al. 2011).

The aim of this study was to prepare the boehmite nanopowder through an environmentally friendly route and to

use it as an adsorbent for chromium ions. Furthermore, equilibrium, adsorption isotherms and kinetics were studied in order to understand the adsorption mechanism of Cr(VI) onto obtained boehmite.

## Materials and methods

### Synthesis of nanocrystalline boehmite

All chemical reagents except distilled water and sodium aluminate solution obtained in the factory "Alumina" Ltd. Zvornik are of analytical grade and were used without further purification. Nanocrystalline boehmite powder was synthesized according to the published procedure (Milanović et al. 2020), from sodium aluminate solution (concentration of 75 g/l  $\text{Na}_2\text{O}_k$ ) prepared from Bayer liquor. Glucose (D-(+)-Glucose, anhydrous, Alfa Aesar, Fisher Scientific, UK) was used as a surfactant, with the molar ratio of  $\text{Al}_2\text{O}_3/\text{glucose} = 1:10$ . The solution was neutralized with the use of 1 M sulfuric acid (Aurubis, Bulgaria). During neutralization procedure, solution was stirred at 70 °C for 60 min. The obtained white precipitate was separated by vacuum filtration, washed with distilled water to remove residual ions and dried at 110 °C for 3 h.

### Batch adsorption experiments

Adsorption experiments were performed in a batch mode by adding 0.1 g of the adsorbent into 200 ml of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution (Centrohem, Serbia) of different initial chromium(VI) ions concentrations (10–1000 mg/l) and pH = 2 adjusted with nitric acid. The mixture was continuously shaken at different time intervals (2 min to 24 h) at room temperature. Adsorbent was separated from the solution by filtration on fiber glass round filter, type MN 85/70 BF, 45 mm (MACHERY–NAGEL, Germany) and in obtained filtrates, residual concentration of chromium(VI) ions was determined by oxidation reduction titrations (Lide 2006). The amount of adsorbed ions per mass of the adsorbent ( $q$ ) was calculated as follows:

$$q = \frac{(C_0 - C)}{m} \quad (1)$$

where  $m$  is the mass of an adsorbent added per liter of solution,  $C_0$  (mg/l) is the initial Cr(VI) concentration and  $C$  is the Cr(VI) concentration after adsorption.

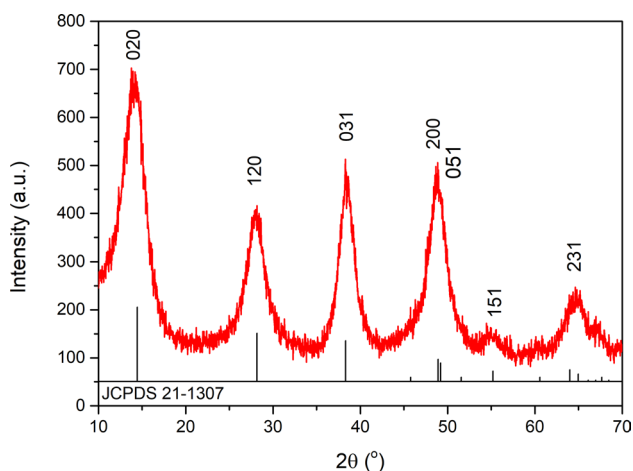
## Characterization techniques

The crystallographic structure of obtained boehmite powder was analyzed by X-ray diffraction (XRD) using Rigaku MiniFlex 600 diffractometer (CuK $\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ) in  $2\theta$  range  $10\text{--}70^\circ$  with a scan rate of  $0.03^\circ/\text{s}$ . The Fourier-transformed infrared spectroscopy (FTIR) was performed on Nicolet-Nexus 670 spectrophotometer in the range  $4000\text{--}400 \text{ cm}^{-1}$ . Adsorption/desorption characteristics of the sample were measured by nitrogen adsorption at 77 K (Micromeritics ASAP 2010 instrument) and specific surface area was calculated by the BET method. Pore size distribution was obtained by fitting the Barret–Joyner–Hallender (BJH) model to the desorption isotherm. The zeta potential of suspension was measured using a Malvern Zetasizer Nano ZS instrument.

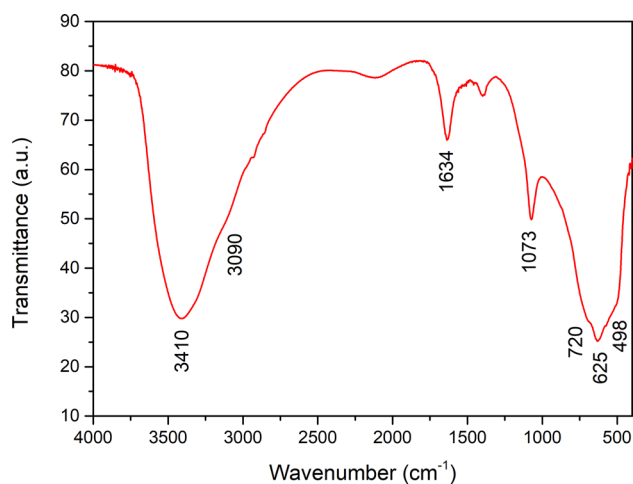
## Results and discussion

### Structural and textural characterization

The XRD pattern of the as-synthesized sample, shown in Fig. 1, refer to the pure boehmite phase with an orthorhombic unit cell (JCPDS No. 21–1307) (Granados-Correa and Jiménez-Becerril 2009; Milanović et al. 2018). The broad peaks indicate a low crystallinity, as well as the nanocrystalline nature of the powder. The bands in the FT-IR spectrum of the sample, Fig. 2, matched with the boehmite phase according to the literature data (Alex et al. 2013; Milanović et al. 2020; Vo et al. 2018), confirming its purity. The band at  $1073 \text{ cm}^{-1}$  and the shoulder at  $3090 \text{ cm}^{-1}$  refer to the (Al)O–H bending and stretching vibrations of boehmite, respectively. FTIR bands at around  $498$ ,  $625$  and  $720 \text{ cm}^{-1}$  correspond to the vibration modes of  $\text{AlO}_6$ . Two prominent



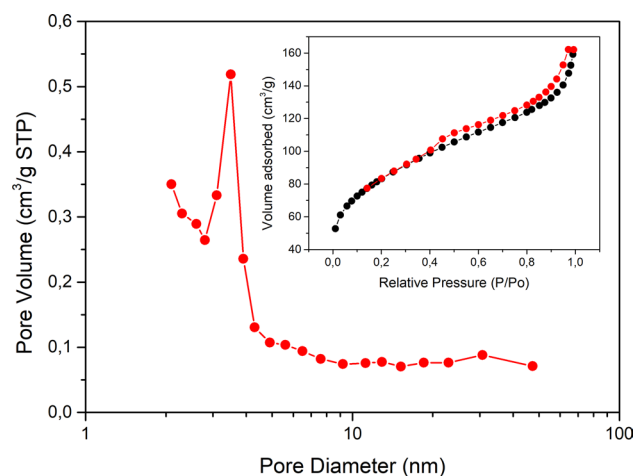
**Fig. 1** XRD pattern of the boehmite nanopowder



**Fig. 2** FTIR spectra of the boehmite nanopowder

bands at  $3410$  and  $1634 \text{ cm}^{-1}$  can be assigned to the OH stretching and HOH bending modes of the adsorbed water, respectively.

The  $\text{N}_2$  adsorption/desorption isotherm and pore size distribution of the boehmite powder are shown in Fig. 3. The isotherm belongs to the type IV which is typical for mesoporous materials while hysteresis loop is of H3 type, according to the IUPAC classification. Such isotherm is characteristic for the aggregates of plate-like particles that have slit-shaped mesopores (Mikhaylov et al. 2017; Mohammadnezhad et al. 2016; Wang et al. 2009). This result is in accordance with our previously published paper (Milanović et al. 2020), where the lamellar framework of the flower-like boehmite nanoparticles is obtained under similar conditions. The slit-shaped pores are about  $3 \text{ nm}$  in width as calculated by the Barret–Joyner–Halenda (BJH) method.



**Fig. 3** Nitrogen adsorption/desorption isotherms and corresponding BJH pore size distribution of the boehmite nanopowder



The BET surface area and total pore volume of boehmite are 296 m<sup>2</sup>/g and 0.23 cm<sup>3</sup>/g, respectively. This large surface area and porous particles that have rough surfaces provide excellent adsorbent characteristics. Namely, the large surface area means there is more surface available for adsorption, which results in greater adsorption efficiency.

### Chromium(VI) adsorption isotherms

In order to investigate the Cr(VI) ions adsorption process onto mesoporous boehmite nanoparticles, adsorption equilibrium studies were conducted. For interpretation of this process, various isotherm models can be used. These models are actually mathematical equations which express a relationship between adsorbed amount of adsorbate and the amount left in the solution in the state of equilibrium. Furthermore, equilibrium constants give more details about mechanism of adsorption or adsorbent affinity toward adsorbate. This information is essential for designing efficient adsorption systems. In this study, most commonly used Langmuir and Freundlich models were applied in their linear form (Table 1).

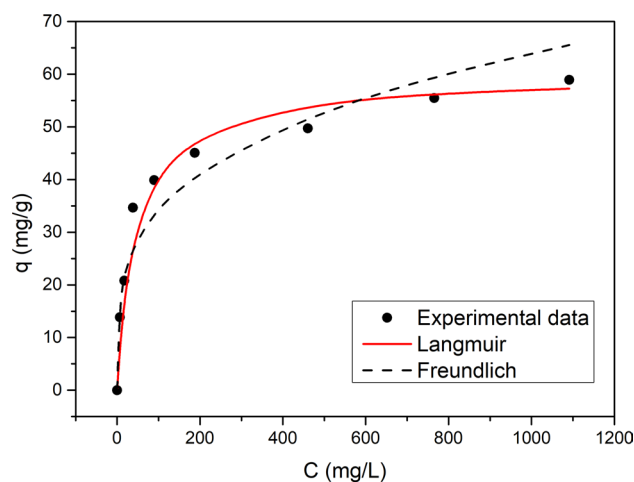
Fitting experimental data to Langmuir model resulted in maximum capacity of 59.5 mg/g and correlation coefficient value of 0.996. Compared to Freundlich correlation coefficient value, high  $R^2$  for Langmuir isotherm indicates that adsorption of chromium(VI) ions follows this model as shown in Fig. 4. Unlike Freundlich model, which suggests heterogeneous surface, Langmuir model assumes the formation of adsorbate monolayer on the homogeneous surface of adsorbent and the absence of interactions between adsorbed molecules (Farouq and Yousef 2015; Kaveeshwar et al. 2018). According to dimensionless separation factor,  $R_L$ , expressed as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (2)$$

it can be determined if the adsorption is linear, favorable, unfavorable or irreversible. Value of  $R_L$  for adsorption of chromium(VI) by mesoporous boehmite is between 0 and

**Table 1** Isotherm models and isotherm parameters for chromium(VI) adsorption by boehmite

Model	Equation	Parameter	Value
Langmuir	$\frac{C}{q} = \frac{1}{K_L q_m} + \frac{1}{q_m} C$	$q_m$ (mg/g)	59.5
		$K_L$ (l/mg)	0.0231
		$R^2$	0.996
Freundlich	$\log q = \log K_F + \frac{1}{n} \log C$	$K_F$ (mg/g)(l/mg) <sup>1/n</sup>	10.3514
		$1/n$	0.2638
		$R^2$	0.9083



**Fig. 4** Langmuir and Freundlich isotherms for chromium(VI) adsorption by boehmite (initial ion concentration 10–1000 mg/l, sample dose 0.1 g per 200 ml)

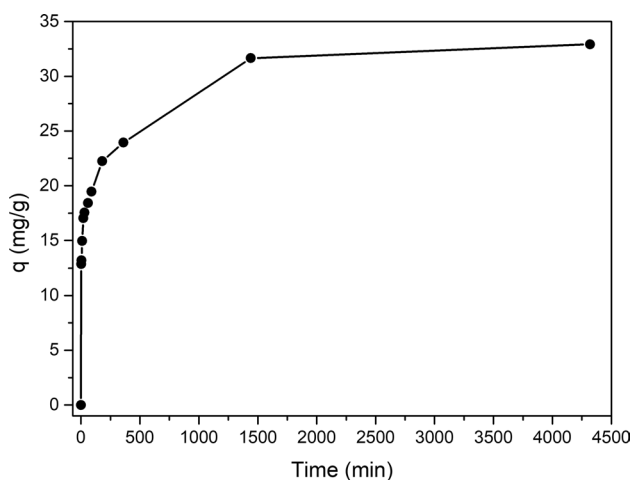
1 which indicates favorable process (Hameed et al. 2008). Moreover, maximum Langmuir adsorption capacity is in agreement with experimentally obtained value (58.9 mg/g) while Freundlich constant  $K_F$ , which also indicates adsorption capacity, is much lower. The obtained results are in agreement with the literature data for alumina-based adsorbents. Li et al. (Li et al. 2016) investigated adsorption of chromium(VI) onto mesoporous alumina and concluded that the process is best described by Langmuir with the maximum Cr(VI) uptake capacity of 46 mg/g. Luo et al. (Luo et al. 2016) and Islam et al. (Islam et al. 2020) reported that adsorption of chromium(VI) ions onto boehmite can also be fitted well with the Langmuir equation reaching adsorption capacities of 12.26 and 66.35 mg/g, respectively. Mikhaylov et al. (Mikhaylov et al. 2017) investigated adsorption of chromium(VI) onto composite  $\gamma$ -AlOOH/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and concluded that the process is best described by the Langmuir equation.

### Adsorption kinetics

The studies of chromium(VI) ions adsorption onto boehmite were also carried out as a function of time. The kinetics of adsorption process is one of the factors that influences the overall efficiency of the process. The experimental results are shown in Fig. 5.

The adsorption of chromium(VI) ions is fast in the first 180 min probably due to a large number of free active sites on the outer surface of the adsorbent particles. After this period, 70% of total amount of adsorbed ions is already bound. The adsorption process continued slowly for the whole period studied. The maximum adsorption capacity obtained after 72 h was 32.92 mg/g. Granados-Correa





**Fig. 5** Adsorption capacity of boehmite for chromium(VI) ions as a function of contact time (initial ion concentration 50 mg/l, sample dose 0.1 g per 200 ml)

et al. (Granados-Correa and Jiménez-Becerril 2009) studied adsorption of chromium(VI) onto boehmite and reported adsorption capacity of only 0.038 mg/g in the state of equilibrium which was reached after only one hour, while Vo et al. (Vo et al. 2018) obtained adsorption capacity of 17.08 mg/g for Cr(VI) by  $\gamma$ -AlOOH after 350 min. The high adsorption capacity of the synthesized boehmite nanoparticles in this work could be explained by the value of zeta potential at the surface of the particles, as well as the nature of Cr(VI) ions present at specific pH. Namely, the measured zeta potential of the boehmite in aqueous solution at pH 2 is about +27 mV. At low pH value, Cr(VI) ions mainly exist in the form of negatively charged  $\text{HCrO}_4^-$  or  $\text{Cr}_2\text{O}_7^{2-}$  ions (Granados-Correa and Jiménez-Becerril 2009; Luo et al. 2016; Vo et al. 2018), so they can easily move toward the positive surface of

the adsorbent owing to the electrokinetic attractive force, thus favoring the adsorption. Furthermore, the adsorption capacity of the synthesized boehmite nanoparticles is higher than most reported alumina-based adsorbents shown in Table 2.

A simple comparison of the synthesis method used in this work with those used in the literature and presented in Table 2 (Cai et al. 2010; Li et al. 2016; Luo et al. 2016; Vo et al. 2018) gives further evidence of the economic and environmental advantages of the obtained nanocrystalline boehmite. The price of the sodium aluminate solution per unit mass is one or two orders of magnitude lower than for precursors usually employed in the sol-gel or hydrothermal synthesis. Also, the time spent on the preparation as well as low energy consumption without the need for high temperature conditions additionally lower the costs and manufacturing environmental footprint. Further on, the synthesis process itself could be incorporated as a side stream of the main Bayer process and use low concentration aluminate solution, thus reducing the amount of waste from the Bayer process but with the additional benefit of obtaining new boehmite product with fine size, high specific surface area and excellent adsorption characteristics. So this material could be regarded as a potentially cheap and environmentally friendly adsorbent for Cr(VI) removal.

For interpreting kinetic data and elucidating a mechanism of chromium ions adsorption onto boehmite, the most commonly used models such as pseudo-first, pseudo-second order and Elovich model were employed (Rziga 2021). The results of experimental data fitting for used models are shown in Table 3. In these equations  $q_e$  indicates adsorption capacity at equilibrium (mg/g),  $q_t$  (mg/g) is the amount of adsorbed ions in a specific period,  $k_1$  is adsorption rate constant of pseudo-first model ( $\text{min}^{-1}$ ),  $k_2$  is rate constant of pseudo-second order model (g/mg min),  $\alpha$  is initial rate of adsorption (mg/g min) and  $\beta$  is desorption constant (g/mg).

**Table 2** Adsorption capacities of chromium(VI) obtained from different adsorbent materials from time dependant adsorption curves

Sorbents	Adsorption conditions	BET ( $\text{m}^2/\text{g}$ )	conc. of adsorbent (g/l)	conc. of Cr(VI) solution (mg/l)	$q_m$ (mg/g)
$\text{Fe}_2\text{O}_3@ \text{AlOOH}$ (Yang et al. 2013)	25 °C, pH 4.0	319.7	0.2	10	21.6
$\gamma$ -AlOOH/PVA granules (Vo et al. 2018)	25 °C, pH 5.5	248	0.1 g	25	35.91
Boehmite/PVA composite membrane (Luo et al. 2016)	25 °C, pH 5.5	/	0.2 g	50	30.97
$\gamma$ - $\text{Al}_2\text{O}_3$ (Cai et al. 2010)	25 °C, pH 3	149	0.8	90	6.7
Activated alumina (Marzouk et al. 2013)	25 °C, pH 5–6	155	80	200	2.53
Mesoporous alumina, MA-F127 (Li et al. 2016)	25 °C, pH 2.5	289	5	50	15.9
$\gamma$ -AlOOH (Vo et al. 2018)	25 °C, pH 5.5	385	0.1 g	25	17.08
Boehmite (Luo et al. 2016)	25 °C, pH 5.5	/	0.2 g	50	11.19
Boehmite (Granados-Correa and Jiménez-Becerril 2009)	25 °C, pH 5.5	224	10	10	0.038
Boehmite, this work	25 °C, pH 2	296	0.5	50	32.9



**Table 3** The values of estimated kinetic parameters for adsorption of chromium(VI) ions onto boehmite

Model		Parameter	Value
Pseudo-first order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$	$q_e$ (mg/g)	33
		$k_1$ (min <sup>-1</sup> )	0.0014
		$R^2$	0.9785
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$	$q_e$ (mg/g)	33.11
		$k_2$ (g/mg min)	0.0009
		$R^2$	0.999
Elovich	$q_t = \beta \ln(\alpha\beta) + \beta \ln t$	$\beta$ (g/mg)	2.8162
		$\alpha$ (mg/g min)	7.3361
		$R^2$	0.9532

The value of  $R^2$  indicates that the pseudo-second order model provides the best fit ( $R^2 = 0.999$ ) while other two applied models showed significantly lower values of correlation coefficient. Moreover, the value of adsorption capacity calculated by the second-order model (33.11 mg/g) is in an excellent agreement with experimentally obtained capacity (32.92 mg/g). This confirms that the model accurately describes the adsorption kinetics throughout the period of experiments. According to the assumptions of the model, adsorption of chromium(VI) ions onto mesoporous boehmite nanoparticles occurs as chemical reaction which could be the rate-controlling step (Ho and McKay 1999).

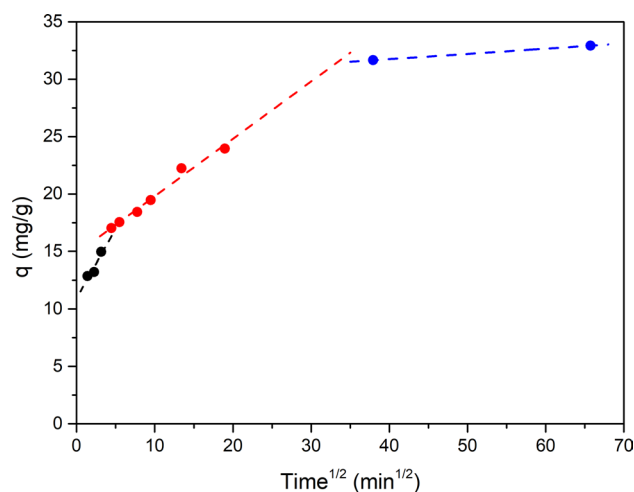
### Adsorption mechanism

Kinetic models do not provide any information about diffusion mechanism so Weber-Morris model was applied in order to gain insight into mechanisms of adsorption and rate limiting step of the process. It is usually expressed as (Weber and Morris 1963):

$$q_t = k_{id}t^{1/2} + C \quad (3)$$

where  $k_{id}$  is intraparticle diffusion rate constant and  $q$  is adsorbed amount of adsorbate at time  $t$ .

According to this model, if a plot  $q_t$  versus  $t^{1/2}$  is a straight line passing through the origin then the only rate limiting step of adsorption process is intraparticle diffusion. The plot for adsorption of chromium(VI) onto boehmite shown in Fig. 6, implies that the process is complex and not governed only by the intraparticle diffusion. Three linear portions can be identified which represent faster



**Fig. 6** Intraparticle diffusion plot for adsorption of chromium(VI) ions onto boehmite

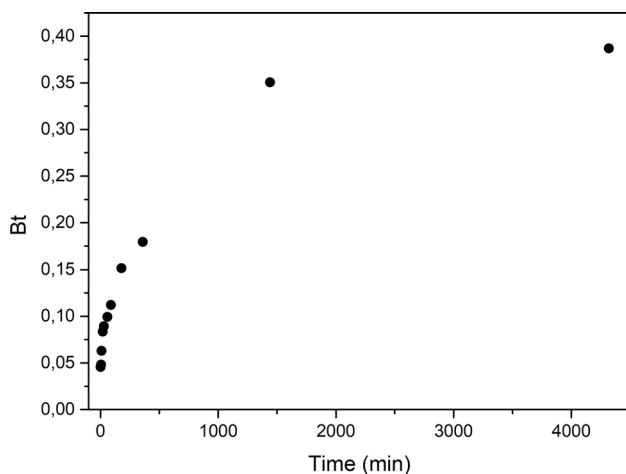
diffusion through boundary layer and adsorption onto outer surface, slower diffusion into pores and adsorption onto inner surface and equilibrium, respectively.

Since the Weber-Morris model suggested that adsorption is complex process, Boyd model (Boyd et al. 1947) was additionally applied:

$$F = 1 - \left(\frac{6}{\pi^2}\right) \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) \exp(-n^2 Bt) \quad (4)$$

where  $F$  is the fractional attainment of equilibrium at different times, and  $Bt$  is function of  $F$  which could be expressed as:

$$F = \frac{q_t}{q_e} \quad (5)$$



**Fig. 7** Boyd's plot for chromium(VI) adsorption onto boehmite

where  $q_t$  and  $q_e$  are adsorption capacities in specific time and equilibrium, respectively. For  $F < 0.85$  Reichenberg's approximation was then used (Viegas et al. 2014):

$$Bt = \left( \sqrt{\pi} - \sqrt{\pi - \left( \frac{\pi^2 F}{3} \right)} \right)^2 \quad (6)$$

This model is based on the assumption that the intraparticle diffusion is rate-controlling step of the process if plot  $Bt$  vs.  $t$  is linear with zero intercept. The plot for adsorption of Cr(VI) is shown in Fig. 7. Its nonlinearity indicates that the film diffusion or chemical reaction might be the rate limiting step (Boyd et al. 1947; Viegas et al. 2014).

## Conclusion

Simple approach for synthesis of boehmite nanopowder is developed. The study shows that at relatively low temperature, it is possible to obtain mesoporous nanocrystalline boehmite powder, with very large specific surface area and appropriate pore size distribution which could have a great potential as an absorbent in water treatment and other adsorption fields. In particular, the results show that thus obtained mesoporous boehmite could be an effective adsorbent for the removal of Cr(VI) ions from aqueous solutions

under the tested experimental conditions. The adsorption kinetics studies suggested that the kinetics rate for the adsorption of Cr(VI) could be best described by the pseudo-second order model and that the sorption process occurs as chemisorption. The maximum adsorption capacity obtained after 72 h was 32.92 mg/g. According to the adsorption isotherm studies, Langmuir adsorption isotherm model fit the experimental data very well with the maximum adsorption capacity of 59.5 mg/g while the experimentally obtained capacity was 58.9 mg/g. Diffusion studies showed that the process is complex and it is probably not governed only by the intraparticle diffusion. Beside the high adsorption capacity, the main advantage of the obtained mesoporous boehmite nanopowder essential for its practical application is straightforward, ecofriendly and cost-effective synthesis. This method has a potential for industrial scale applications where it could save time and offer energy efficient synthesis of high-quality boehmite while reducing environmental footprint of the process.

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## Declarations

**Conflict of interest** All authors declare that they have no conflict of interest.

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