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Removal of Cr(VI) from contaminated water using soil rich in kaolinite - ferrinatrite, coffee husk ash and soil rich in kaolinite – goethite: characteristic, isotherm and kinetic study

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ABSTRACT

This study examined the efficiency of Cr (VI) ion removal from contaminated water using locally available adsorbent media. Equilibrium contact time for Cr (VI) removal was observed within 40 min. Adsorption of Cr (VI) followed pseudo second-order kinetics with $R^2 > 0.99$ for the three adsorbent media. Results of the adsorption isotherm show that the Freundlich adsorption isotherm model better described Cr (VI) adsorption into soil rich in kaolinite–ferrinatrite (SRKF), soil rich in kaolinite–geothite (SRKG) and coffee husk ash (CHA) with correlation coefficients; $R^2 > 0.93$. The adsorption capacity of the adsorbent can be arranged in the order of decreasing CHA > SRKG > SRKF. These adsorbent materials could be used for the removal of Cr (VI) from wastewater. However further investigation will be required for practical application of these locally available adsorbent materials for removal of chromium from wastewater.

Keywords: Adsorption; Adsorption capacity; Chromium (VI); Kinetics; Isotherm

1. Introduction

The release of toxic chemicals from industrial wastewater into the environment degrades water quality and is hazardous to human beings, as well as other living organisms such as aquatic life [1–3]. Cr (VI) is generated from different industrial activities carried out in textile industries, leather tanning, electroplating, steel production, paint manufacturing, pulp processing, chromate preparation, electric and electronic components [4–6]. According to United State Environmental Protection Agency [7], Cr (VI) is the most prioritized poisonous pollutant [8]. Chromium is found mostly in the form of chromium (III) and chromium (VI). chromium (VI) is 100 times more poisonous than chromium (III) when found on the surface and in ground water [8]. According to the World Health Organization (WHO), the recommended maximum tolerable limit of chromium (VI) in wastewater discharged from industries is 0.25 mg L^{-1} [9]. Thus, it is critical to find effective ways to remove chromium (VI) from industrial wastewater. Typical treatment technologies used to remove chromium from contaminated water include ion exchange, chemical reduction, adsorption, chemical precipitation, membrane separation, reverse osmosis, and electro coagulation. Of all the treatment technologies, adsorption technique is one of the most feasible and promising technique, because of its wide raw material sources, low investment cost, high efficiency, effectiveness, flexibility in design and easy operation [6,8–11]. Thus, suitable wastewater treatment technology using locally available natural materials that may be used in developing countries such as Ethiopia remains an important issue to address. Among the natural adsorbents, soil rich in kaolin-

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ite-ferrinatrite (SRKF), coffee husk ash (CHA) and soil rich in kaolinite-goethite (SRKG) would meet the conditions that have been established for the wastewater treatment process due to its abundant availability in Ethiopia and suitable physical and chemical properties.

The objective of this study was to investigate the efficiency of Cr (VI) ion removal from contaminated water, determine the adsorption kinetics and the isotherms, as well as the contact time by using low-cost locally available materials under a batch adsorption experiment.

2. Materials and methods

2.1. Sample collection

Soil rich in kaolinite–ferrinatrite (SRKF), coffee husk ash (CHA) and soil rich in kaolinite – goethite (SRKG) are abundantly found in Ethiopia. The samples were collected from four localities from Jimma Zone, Oromia Regional National State, South-west Ethiopia. The collected samples were mixed in a ratio 1:1 to make a composite sample.

2.2. Physical characteristics

The physical characteristics of the adsorbent materials used for the present study are shown in Table 1. This was characterized at the Ethiopia Institute of Agricultural Research by document number: Ethiopian Institute of Agricultural Research (EIAR/F). 510-2, in February 2015. The physical characteristic of locally available materials was performed using standard procedures. Characterization of the locally available materials was carried out through electrical conductivity, cation exchange capacity, pH, organic carbon, and organic matter.

2.3. Chemicals

The stock ($K_2Cr_2O_7$) standard solution of each of Cr (VI) (500 mg/L, 1000 mg/L) for adsorption experiments were prepared by dissolving 1.414 g and 2.828 g of $K_2Cr_2O_7$ (FINKEM) in 1000 mL distilled water in a volumetric flask, respectively. Working solutions were prepared by appropriate dilution of the stock solution immediately prior to their use.

2.4. Batch adsorption procedures

Sets of series of duplicate batch adsorption experiments were conducted at room temperature by shaking a mixture of a known concentration of the adsorbate and a desired dose of adsorbents at a defined (i.e. 100, 150, 200 and 250 rpm) on a horizontal shaker. Optimum agitation speed was determined after conducting a preliminary study. Optimum contact time was determined by agitating a mixture of 0.4 g adsorbent and 3.5 mg/L Cr (VI) concentration on a horizontal shaker at 150 rpm for SRKG and SRKF, whereas at 100 rpm for CHA for over 120 min. Equilibrium adsorption isotherm was examined by varying the concentration of the adsorbate from 10 to 60 mg/L and maintaining the dose of the three adsorbent materials at 0.35 g and shaking speed at 100 and 150 rpm for CHA, and SRKG and SRKF respectively. In all the adsorption experiments, the pH of the solution was maintained at 2.0.

2.5. Desorption experiment procedure

The reusability of the exhausted adsorbent material was investigated first by allowing 2 mg/L Cr(VI) to be adsorbed onto 0.35 g adsorbent dose for all the three adsorbent materials at optimum contact time. Second, the exhausted solid adsorbent materials were separated from the supernatant solution through filtration and allowed to be dried in an oven at 105°C overnight. Third, the oven dried, exhausted adsorbate media were added into 0.01, 0.1 and 0.5 M NaOH desorbing solution separately. The mixtures were agitated under the same experimental conditions used for adsorption experiments. Finally, the amount desorbed was determined using Eq. (1) is given below [12]:

$$Desorption\,ratio\,(\%) = \frac{Amount\,of\,desorbed}{Amount\,of\,adsorbed} * 100 \tag{1}$$

3. Results and discussions

3.1. Batch adsorption experiment

The batch adsorption technique expanded with the new natural sorbent (SRKF, CHA and SRKG) in this work, for chromate removal was carried out with aqueous solution and actual real water. A series of duplication of the experiment was executed at 22 ± 2°C at the Jimma University, Environmental Health Laboratory in 2016. Polyethylene plastic bottles were washed using HNO_3 and thoroughly rinsed with distilled water. Each set of the batch adsorptive experiment effect contained duplicate trial, blank (only SRKF, CHA or SRKG) and control (only Cr (VI) ion). A series of 300 mL plastic bottles were readied for experiments with a 100 mL aqueous solution containing a known Cr (VI) ions concentration. Thereafter an

Table 1
Physical characteristic of the adsorbent materials

Sample	Parameters									
	EC (μs cm^{-1})	CEC (cmol Kg^{-1})	pH (%)	TN (%)	OC (%)	OM (%)	Sand (%)	Silt (%)	Clay	Texture
SRKF	22.80	24.00	5.24	0.14	0.75	1.28	18.80	10.40	70.80	Clay
CHA	64.30	36.20	12.47	–	0.518	0.893	–	–	–	–
SRKG	20.10	21.50	4.56	0.13	0.61	1.05	12.80	10.40	76.80	Clay

EC: electrical conductivity; CEC: cation exchange capacity; TN: total nitrogen; OC: organic carbon; OM: organic matter adjusting pH by placing Polyethylene plastic bottles containing the desired adsorbent dose was carried out by agitating at a fixed rpm on a Horizontal Thermostat Orbital shaker for a fixed contact time and at room temperature. The solid (SRKF, CHA or SRKG) was then separated from the solution using Whatman filter paper (0.45 μm). Then, 0.2 N H_2SO_4 for pH adjusted to pH 1 ± 0.3 and then, added 1 mL diphenyl-carbazide in 50 mL was added. It then stood for 10 min for color development. Residual Cr (VI) ion concentration was transferred to 1 cm absorption cell and determined using the UV-visible spectrophotometer (HACH LANGE © model No: 5000). The average of duplicate measurements was reported. Origin 8 software was used to perform the statistical data analysis of the studies. The value of chromium (VI) adsorbed over the unit mass of the adsorbent media, and the percentage adsorption was computed using Eqs. (2) and (3) given below, respectively [3].

$$q_t = \frac{(C_o - C_t)}{m} * V \tag{2}$$

$$A = \frac{(C_o - C_t)}{C_o} * 100 \tag{3}$$

where C_0 (mg L^{-1}) and C_t (mg L^{-1}) are initial *Cr* (VI) ions concentration and concentration of *Cr (VI)* ion after an adsorption time t, respectively; *V (L)* is volume of the aqueous solution; and *M (g)* the mass of LAM; while q_t (mg·g^{-1}) and *A* (%) are the value of Cr (VI) ions adsorbed. Finally, selected optimum effect depends on removal efficiency of Cr (VI) for further experiments

3.2. Contact time

The effect of contact time on chromium (VI) adsorption influence on soil rich in kaolinite-ferrinatrite was studied by continuously increasing the contact time from 10 to 120 min (Fig. 1). As can be seen in Fig. 1, the adsorptive removal of adsorbate increased with an increase in contact time until 40 min. After 40 min (equilibrium point), the adsorption removal of adsorbate remained constant due to binding sites exhaustion [13]. The rate of adsorption of chromium (VI) ion was high up to 40 min. This was due to locally available materials (LAM) such as SRKF, CHA and SRKG which surfaces having many open spaces that could lead to strong attraction forces between Cr (VI) and an adsorbent – this is confirms an observation by Wanees et al. [14]. Adsorptive removal of chromium (VI) from 10 and 40 min was high due to highly increased adsorption sites [15]. After 40 min there was no change in the rate of adsorption of Cr (VI) on LAM. This showed that LAM did not have sufficient open space due to the fact that the bulk solution increased. This finding agreed with the observation by Workneh et al. [16]. The adsorption capacity was high for a short period (40 min) on LAM adsorbent. The reason for this could be due to the open space, clay texture, lower bulk density, and small particle size. This finding agrees with the finding repeated by Babel and Opiso [17]. The value of the contact time of 40 min was taken as a maximum for further studies.

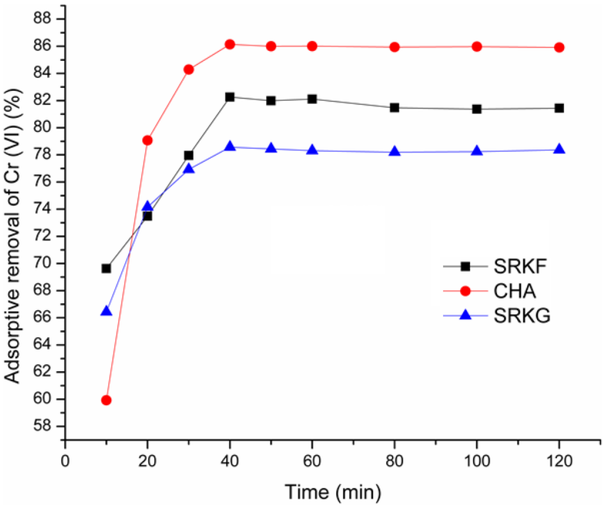

Fig. 1. Cr (VI) adsorption on SRKF (squares), CHA (circle) and SRKG (triangles) were condition temperature 22 ± 2°C, and pH = 2.

3.3. Kinetic model of adsorption

The results showed that the pseudo-second order equation best described the kinetic mechanisms of chromium (VI) ions adsorption. This is evident from the higher determination coefficient value ($R^2 > 0.99$ for all LAM). In addition, the predicted equilibrium adsorption capacities were quite close to the experimental values for all particle sizes tested in this study, confirming the validity of the pseudo second order rate assumption. The transports of chromium (VI) ions from solution through the particle solution interface into the pores of the particles as well as the adsorption on the available surface of SRKF, CHA and SRKG were responsible for the adsorption of the hexavalent chromium ions.

3.4. Isotherm model of adsorption

The adsorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the adsorbent, at room temperature and pH. Analysis of the relationship between the adsorption capacity of the materials (SRKF, CHA and SRKG) and chromium (VI) ions' initial concentrations at equilibrium was performed using two most frequently employed models: the Langmuir and Freundlich models. These models can be used to design and optimize an operating procedure. The data from these models provide information to predict removal of Cr (VI) ions to the adsorbents, and an estimation of the adsorbent amounts needed to remove the hexavalent chromium ions from the solution. In all cases, the result confirms that the Freundlich adsorption capacity of SRKF is greater compared to that of SRKG. The essential characteristics of the Langmuire isotherm may be expressed in terms of the dimensionless separation factor values (R_L) value. In all cases, the R_L values for the experimental data is between 0 and 1, which is also an indicator of the favorable adsorption of Cr (VI) ions on the SRKF, CHA and SRKG. In all experiments, the larger value of K_L, obtained for the chromium (VI) ions SRKF, indicate the strong interactions between the hexavalent chromium

Table 2
Summary of linear estimated kinetic parameters for adsorption of Cr (VI) ions onto adsorbents

Adsorbents	Pseudo first-order: Log (q_E–q_T) = log q_E–k_1/2.303*T			Pseudo second-order: T/q_T = 1/$k^2q_E^2$ + 1/q_E *T		
Ads.	log q_E	k_1/2.303	R^2	1/$k^2q_E^2$	1/q_E	R^2
SRKF	0.202	0.0006	0.5181	3.3233	1.366	0.9985
CHA	0.1915	0.0008	0.3308	2.8739	1.296	0.999
SRKG	0.1824	0.0002	0.4828	0.9735	1.4485	0.9999

Table 3
Summary of linear estimated isotherm models and its constant value for chromate adsorption

Adsorbents	Freundlich Isotherm: Log q_e = log K_F + 1/n logC_e			Langmuir Isotherm: 1/q_E = 1/q_M + 1/q_MK_L*1/C_E		
Ads.	K_F (mg g^{-1})	1/n	R^2	1/q_M (mg g^{-1})	1/q_Mk_L	R^2
SRKF	1.2114	0.4867	0.9336	0.1089	0.0057	0.9139
CHA	0.9025	0.5538	0.9846	0.0746	0.1028	0.9444
SRKG	0.9925	0.6927	0.978	0.0996	0.0348	0.9576

ions and SRKG and CHA. The conclusions are in conformity with the results obtained in the characterization of the adsorbents which show that CHA has a larger CEC and EC than other two.

3.5. Desorption

The results of desorption experiments show that the amount of Cr(VI) desorbed increases from 35 to 82% for SRKF, from 34 to 77% for SRKG and from 17 to 83% for CHA when the concentration of desorbent increased from 0.01 to 0.5 M NaOH. This indicates that when NaOH is at about 0.5 M concentration, the exhausted adsorbent materials can be regenerated for reuse. However, the regeneration cycle and adsorption capacity of the regenerated adsorbent materials requires further investigation.

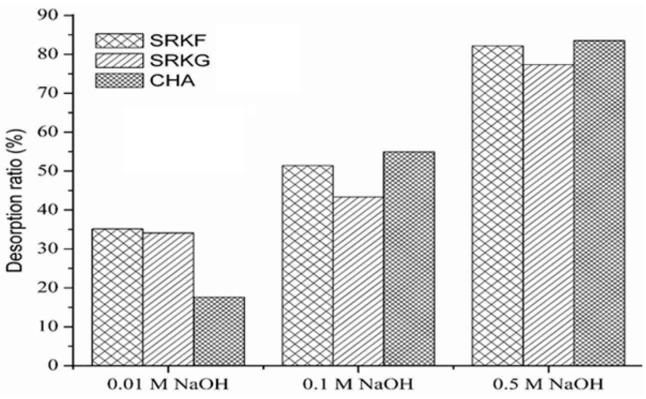

Fig. 2. Cr (VI) desorption on SRKF, CHA and SRKG were condition temperature 22 ± 2°C, and pH = 2

4. Conclusions

The present of chromium (VI) in the water at levels greater than the permitted limit is toxic and can lead to a number of health problems. The present study demonstrated the adsorptive efficiency of SRKF, CHA and SRKG for Cr (VI) ions removal technique from contaminated water. Batch adsorption by different effects, such as the solution pH effect and contact time effect, was evaluated. The Freundlich and Langmuir isotherm was examined in this study at a room temperature of 22 ± 2°C. Therefore, this behavior suggested that LAM can be used as an interesting low-cost adsorbent technology for Cr (VI) removal from contaminated water.

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