Removal of organic dye and toxic hexavalent chromium ions by natural clay adsorption

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ABSTRACT

Organic dyes and toxic heavy metals are among the most serious environmental pollutants and pose a great concern to human health since they are not biodegradable. This paper reports the application of modified natural clay minerals in removal of toxic chromium (VI) ion and methyl-red dye from aqueous solution. Three different types of clay minerals namely Zemero, Seladengay and Mehal Meda clays were collected from different parts of North Shoa Zone, Amhara region, Ethiopia, and then their surfaces were separately modified with different amount of hydrochloric acid (15%, 20%, and 25%), nitric acid (15%, 20%, and 25%) and sulfuric acid (15%, 20%, and 25%). The concentration of chromium (VI) was determined using Atomic Absorption Spectroscopy before and after treatment with the activated clay minerals. UV-Visible Spectrophotometer was used to determine concentration of dyes before and after treatment of the methyl red solution with modified clays. The results demonstrated that Zemero clay mineral modified with 25% of H_2SO_4 was more efficient in removing methyl-red from aqueous solution compared to Seladengay and Mehal Meda clay minerals activated with the same acid under similar conditions. Chromium (VI) ion (96.99%) and methyl-red (99.33%) from aqueous solution were removed by sulfuric acid modified Zemero clay, indicating the potential of the clay minerals for removal of toxic chemicals from water.

Keywords: Adsorption; Acid activation; Clays; Methyl-red; Chromium(VI)

1. Introduction

The effluents discharged from industries and waste treatment processes contain lots of toxic heavy metals, dyes and other chemicals, which are mostly introduced into air, soil and water bodies like rivers, lakes, and oceans. These activities are consequence of industrialization and urbanization, which result in serious deterioration of the quality of air, soil and water [1,2]. Heavy metals and dyes are non-biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [3]. They can enter human body through different ways such as food, drink and air, and thus affect human health. The polluted water has an immediate effect especially when it is consumed directly. Lead, cadmium, copper, zinc, mercury, chromium, and nickel are some of the heavy metals that are considered as the main contaminants of surface water, groundwater, and soils. Some of them can be even toxic at low concentration and have a tendency to accumulate in the food chain [4]. Among all, chromium (VI) is one of the most common toxic heavy metals to all life forms, but used in various industries including ink manufacturing, dyes, paints, metal plating, automobile spare parts, and petroleum refining [5]. Long-time exposure to this hexavalent chromium through different ways like inhalation, ingestion, and skin contact causes irritation and corrosion of skin, respiratory tract, and in some cases cancer and other deadly consequences [6–8].

On the other hand, with the increasing use of dye to color products in several industries including textiles, rubber, paper, plastics, leather, cosmetics, food and mineral processing industries, large volume of effluents contain-

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ing colored solutions, dissolved organics, inorganic solids and suspended solids are generated and eventually discharged to the environment [9]. Particularly wet finishing process, in the textile industry, uses large amount of dye that results in a significant volume of wastewater generation containing high concentration of dyes. Approximately 10–15% dyes remains unfixed and is discharged with the effluent [10]. Reports have indicated that dyes can cause environmental pollution and serious health risks [11,12]. They have also an adverse impact on growth of aquatic plants since they reduce their efficiency of photosynthesis [13]. Therefore, it is an important issue to remove the toxic heavy metals and dyes to reduce their uptake by plants, animals, and humans as well as to prevent them not to pollute water bodies. Numerous approaches that could be used to remove/reduce dye and toxic heavy metals from industrial wastewater have been reported such as traditional methods (chemical-physical treatments, and biological process) and advanced methods (electrochemical interaction, ion pair extraction, membrane filtration and oxidation) [14–18]. However, all these processes are costly and cannot be used by small industries to treat the wide range of dye wastewater [19]. Adsorption has been recognized as a potential and preferred technique for the removal of heavy metals and dyes from wastewater due to its simple and flexible design, low cost and easy operation. For instance reports have shown that peanut shell and chitosan based adsorbent demonstrated high adsorption tendency for the removal of Cr(VI) from the aqueous solution [20–22]. Moreover the adsorption process may generate little or no toxic pollutants and requires low initial capital and operating costs [19], does not produce any sludge [23] and has a superior efficiency compared with conventional processes [24]. Activated carbon is widely used and efficient adsorbent but very expensive and has high operating costs [23].

Clay minerals such as bentonite, kaolin, silica beads, alunite, perlite and zeolite are also important materials which have been considered as low-cost adsorbents for the removal of dyes and toxic heavy metal from wastewater [25,26]. They are effective natural adsorbents due to their small particle sizes, lamellar structures, and negatively charged surfaces which make them good cation adsorbents with large reactive surface areas [27]. Among these clay minerals, bentonite is one of the most extensively used adsorbents [28]. The adsorption capacity of clay minerals can be improved by modification through physical and chemical processes. Their unique properties such as high surface area and surface chemistry, structural properties, chemical and mechanical stabilities make them to have a broad range of applications [29]. Several clay minerals are available in large quantities in Ethiopia which have not been examined for such kind of purposes. Some of the minerals namely Zemero, Seladengay and Mehal Meda clays were used as binder for charcoal briquette preparation in our earlier reported work [30]. However, no work has been reported so far for removal of dyes and heavy metals using these clay minerals. Based on the above facts, we thought that these minerals might have good adsorption properties and could be applied to industrial waste water treatment. Thus, this paper reports the application of modified natural clay minerals in removal

of dyes and heavy metals by adsorption mechanism. As per our expectation, the clay minerals have demonstrated high performance in removing both dyes and toxic chromium (VI) from aqueous solutions.

2. Material and methods

2.1. Chemical and reagents

All chemicals and reagents were of analytical grade, and used as received without any purification. Nitric acid (HNO_3, >69%), sulfuric acid (H_2SO_4, >98%), hydrochloric acid (HCl, >37%), sodium hydroxide (NaOH, >98%), potassium dichromate ($K_2Cr_2O_7$, >99.70%) and Methyl-Red (IUPAC name; 2-(N,N-dimethyl-4-aminophenyl) azobenzenecarboxylic acid with molecular formula $C_{15}H_{15}N_3O_3$, MW: 269.30 g/mol), also called C.I. Acid Red 2, is an indicator dye that turns red in acidic solutions.

2.2. Instruments

2.2.1. UV-Visible spectrophotometer

Absorption was recorded over 200–800 nm using a UV/Visible spectrophotometer (SANYO, SP65, GALANAKAMP, UK) to determine concentration of dyes before and after treatment of the methyl red solution with modified clays.

2.2.2. Atomic absorption spectroscopy

After calibration was made with standard Cr(VI) solution, the concentration of Cr(VI) ion in aqueous solution was determined using atomic absorption spectroscopy instrument (BUCK, Model-210VGP, Method Air/acetylene, wavelength, 357.9 nm, slit width 0.2 nm, energy 71.5, lamp current 4 mA, detection limit 0.01 ppm).

2.2.3. Fourier transform-infrared spectrometer

The FTIR spectra of natural and activated Zemero clay samples were recorded with KBr pellet method using FTIR spectrometer (Perkin Elmer) in the wave number range of 400–4000 cm⁻¹.

2.3. Preparation of modified natural clay

Clay minerals were collected from three specific places of North Shewa Zone, Ethiopia namely Mehal Meda, Seladengay, and Zemero. Each clay samples was ground and washed with distilled water to remove impurities. Then, the mixtures were stirred and the slurries were decanted leaving behind impurities such as sand and stones. The clay samples were dried in the oven at 105°C for 8 h separately. Then the clay samples were modified with sulfuric acid (15%, 20%, and 25%), hydrochloric acid (15%, 20%, and 25%) and nitric acid (15%, 20%, and 25%). Each clay samples (10 g) (Zemero, Mehal Meda and Seladengay) was separately mixed with 100 mL of 15%, 20% and 25% HNO_3, H_2SO_4, and HCl in a separate conical flask. Each of the resulting mixture was heated at 90°C under reflux for

30 min with continuous stirring, and then cooled, filtered under vacuum followed by washing repeatedly with distilled water. The filtered samples were dried at 105°C for 2 h. All the acid activated clay samples were again crushed to a particle size that would pass through a 350 μm mesh size. The activated clays (Zemero, Mehal Meda and Seladengay, hereafter named as ZcAd, McAd, and ScAd clays respectively) were kept in separate polyethylene bags for further experiment.

2.4. Batch adsorption studies of chromium

A stock solution of Cr(VI) (200 ppm) was prepared from potassium dichromate ($K_2Cr_2O_7$) using distilled water, which was further diluted for preparation of test solutions. The adsorption of chromium (VI) onto each modified/activated clay (ZcAd, McAd, and ScAd) was studied in the following way. Prior to batch adsorption, the most efficient clay was identified by treating each modified clay separately with methyl red solution at constant concentration, temperature, clay dosage, contact time and pH. All the rest of the experiments were carried out using the clay mineral that demonstrated high efficiency. Thus ZcAd was found to be the most efficient compared to others and chosen to be used in batch adsorption test of chromium (VI) and methyl-red. Batch adsorption experiments were conducted with ZcAd by varying concentrations of chromium (VI) from 20 to 100 ppm at constant adsorbent dose, contact time, pH and agitation speed. Adsorbent dosage was varied from 0.5 g to 2 g at optimized concentration and constant contact time and pH. The effects of contact time and pH were studied with Cr(VI) at optimized concentration and adsorbent dosage. Contact time and pH were varied from 1 to 4 h, and 2 to 8 value respectively. In all cases required quantity of the adsorbent (ZcAd) was added to 50 mL of chromium (VI) solution. The mixture was shaken in a mechanical shaker with a constant agitation speed of 200 rpm at room temperature for a desired time. The supernatant was separated by centrifugation at 200 rpm and the residual concentration in the supernatant was determined. The metal concentration before and after adsorption in the samples was determined by atomic absorption spectrophotometer. The chromium (VI) percent removal by the adsorbent was calculated as:

$$\% \, Absorption = \frac{C_b - C_a}{C_b} \times 100 \tag{1}$$

where C_b is concentration of chromium (VI) before adsorption, C_a is concentration of chromium (VI) after adsorption. Maximum absorption wavelength (λ_{max}) of untreated methyl-red was determined over scanning from 200 nm to 800 nm by 20 wavelength interval using UV-Vis spectrophotometer. The λ_{max} was found to be 420 nm.

2.5. Adsorption studies of methyl-red

2.5.1. Preparation of aqueous solution of methyl-red

Following the preparation of stock solution, 10 ppm, 20 ppm, 30 ppm and 40 ppm of working solution were prepared through serial dilution from the stock solution.

In order to determine the absorption kinetics, Methyl-red (MR) solution (30 mL, 30 ppm) and 1 g of activated Zemero clay with 25% H_2SO_4 was placed in a 250 mL conical flask. The pH of the solution was adjusted at 4 and agitated at 200 rpm by rotary shaker for 30 min to obtain adsorption equilibrium. 2.5 mL of the sample was taken from the solution in 5 min interval continuously up to 25 min. The suspension was centrifuged at 3000 rpm for 10 min and filtered to remove the clay particles. The absorbance of MR solution was measured and the concentration of MR at time t (C_t) was determined. Finally the graph that indicates absorbance versus time was generated.

3. Results and discussion

3.1. Adsorption studies of chromium (VI)

The three natural clays were modified with 25% of H_2SO_4 and their ability of Cr(VI) removal were investigated under the same conditions, and the results were compared with each other. All the three clay minerals showed very high adsorption capacities (more than 90%), revealing their future prospect of application in different areas. The adsorptions of Cr(VI) ions are 90.05. 92.38, and 96.99% for modified Mahel Meda, Sela Dengay and Zemero clays respectively as indicated in Fig. 1. The activated Zemero clay demonstrated the highest capacity to remove Cr(VI) ion from aqueous solution, indicating its adsorption efficiency. There are factors that affects the Cr(VI) and dyes removal efficiency by clay minerals, for instance temperature, contact time, clay dosage, and clay quality. In order to determine the effect of all these parameters on dye and Cr(VI) adsorption onto clay minerals, we only considered the clay mineral with the highest efficiency (modified Zemero clay, ZcAd).

3.1.1. Effect of pH

The pH of the solution is an important factor that affects the adsorption of metal ions, the chemistry of adsorbent and adsorbate in solution. The removal ability of ZcAd clay was examined at different pH (ranging from 2 to 8) of aqueous solution of Cr(VI) while making other parameters such as constant contact time, dosage of activated clay, temperature and concentration of Cr(VI) fixed. The adsorption of Cr(VI) ions onto the ZcAd clay as a function of pH is presented in Fig. 2. It was observed that the adsorption capacities of ZcAd clay decreased significantly with increasing pH of the solution, i.e. the amount
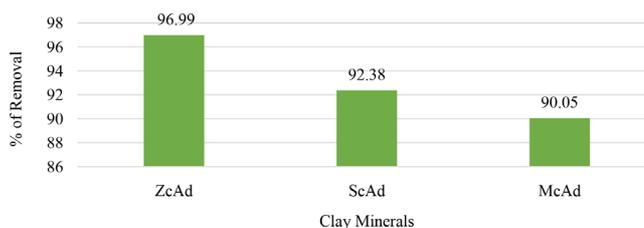
Fig. 1. Chromium (VI) ion removal from aqueous solution by sulfuric acid modified Zemero (ZcAd), Seladengay (ScAd), and Mahel meda (McAd) clays.
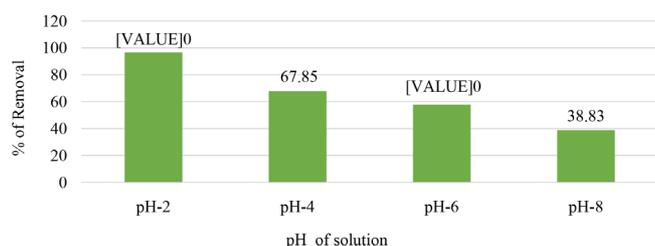
Fig. 2. Effect of pH on the adsorption of Chromium (VI) ions onto activated Zemaro clay.

of chromium ion adsorbed onto the clay decreased as the pH of the solution increased. Percentage adsorption of Cr(VI) onto ZcAd clay at pH-2, pH-3 pH-4 and pH-8 were found to be 96.5, 67.85, 57.7, and 38.83% respectively (Fig. 2). Highest adsorption was achieved at pH-2. It is noted that the dominant form of Cr(VI) at low pH is $HCrO_4^-$ as well as large number of H^+ ions present at this pH that causes the adsorbent surface positively charged, thereby enhancing the adsorption due to electrostatic attraction. Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms such as CrO_4^{2-} and $Cr_2O_7^{2-}$. The decrease in removal at higher pH may be due to abundance of OH^- ions causing increased hindrance to diffusion of dichromate ions [31,32]. Report also indicated that several adsorbents such as wool, olive cake, sawdust, pine needles, almond, coal, and cactus leaves demonstrated a maximum adsorption of Cr(VI) at pH 2.0 [31] which is in agreement with our result.

3.1.2. Effect of contact time

To investigate the effect of contact time on adsorption of Cr(VI) onto ZcAd clay at initial metal ion concentrations (20 ppm) where a maximum percentage of Cr(VI) ions' removal was observed, we varied the contact time from 1 to 4 h while keeping other parameters constant. Fig. 3 shows the removal of Cr(VI) as a function of time. At the beginning, the modified clay showed rapid rate of adsorption of the Cr(VI) ions, however it gradually slowed down and finally reached equilibrium. The amount of ions removed increased from 84.39 to 93.22% as the contact time increased from 1 to 2 h, and improved to 95.31% as the time further reached 3 h. Beyond 3 h, no change in adsorption was observed. The initial fast rate of adsorption is due to availability of a large number of vacant surface sites as well as the larger surface area for adsorption, and after a certain time, the vacant get exhausted and thus lead to decrease in removal of Cr(VI) ions [29].
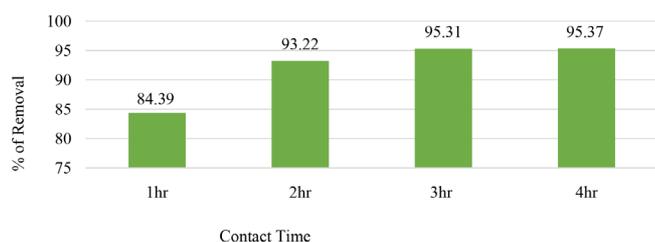
3.1.3. Effect of Cr(VI) concentration

The effect of heavy metal ion concentration on the adsorption performance of ZcAd clay was investigated by varying the concentration of metal ions from 20–80 ppm as indicated in Fig. 4. It is an important parameter in adsorption since a certain amount of adsorbent can adsorb different amount of metal ions at different concentration. The amount of Cr(VI) removal at 20, 40, 60, and 80 ppm are 96.99, 72.52, 69.98 and 67.53% as indicated in Fig. 4. The extent of Cr(VI) ion removal was higher at lower concentration than at higher concentration, suggesting that the percentage of adsorption of Cr(VI) ion onto clay decreases as concentration of adsorbate increases. However, the actual amount of Cr(VI) ions adsorbed per unit mass of the adsorbent increased as the concentration of Cr(VI) ions increased in the test solutions as demonstrated in Fig. 4. At low concentration the ratio of adsorption sites to the total metal ions in the solution is high and hence all metal ions interact with the adsorbent and ions are removed quickly from the solution. With an increase in the number of metal ions, the situation changes and the number of ions available per unit volume of the solution rises. This results in an increased competition for the adsorption sites that cause a decrease in percentage adsorption at high metal ion concentration [27,33].

3.2. Adsorption studies of methyl-red dye

3.2.1. Initial concentration of methyl-red dye

The influence of initial concentration of methyl-red was determined by performing the adsorption experiments at different initial concentration of methyl-red aqueous solution (10–40 ppm) as indicated in Fig. 5a. The effect of the initial dye concentration depends on the immediate relation between the dye concentration and the available binding sites on an adsorbent surface. Zemero clay activated with 25% sulfuric acid (0.5 g) was mixed with methyl-red solution of different concentrations such as 10, 20, 30 and 40 ppm (10 mL from each) in conical flask and shaken using rotary shaker at 200 rpm for a fixed time, pH and temperature. The amounts of dye percent removal versus varying initial dye concentrations were plotted in Fig. 5a. The optimum value of the initial dye concentration was found to be 30 ppm. As the dye concentration increased up to certain amount, the percentage of dye removal increased. This can be attributed to an increase in the driving force or increased concentration gradient between the solution and adsorbent in accordance with the law of mass action (acts as a driving force for the transfer of dye molecules from the solution to

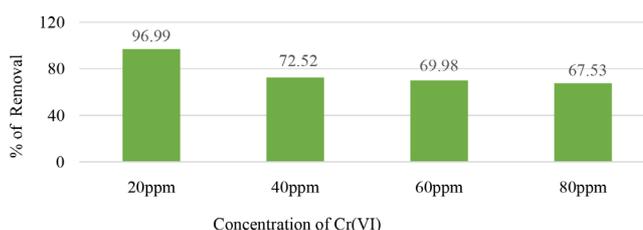Fig. 3. Effect of contact time on Chromium (VI) ions removal.

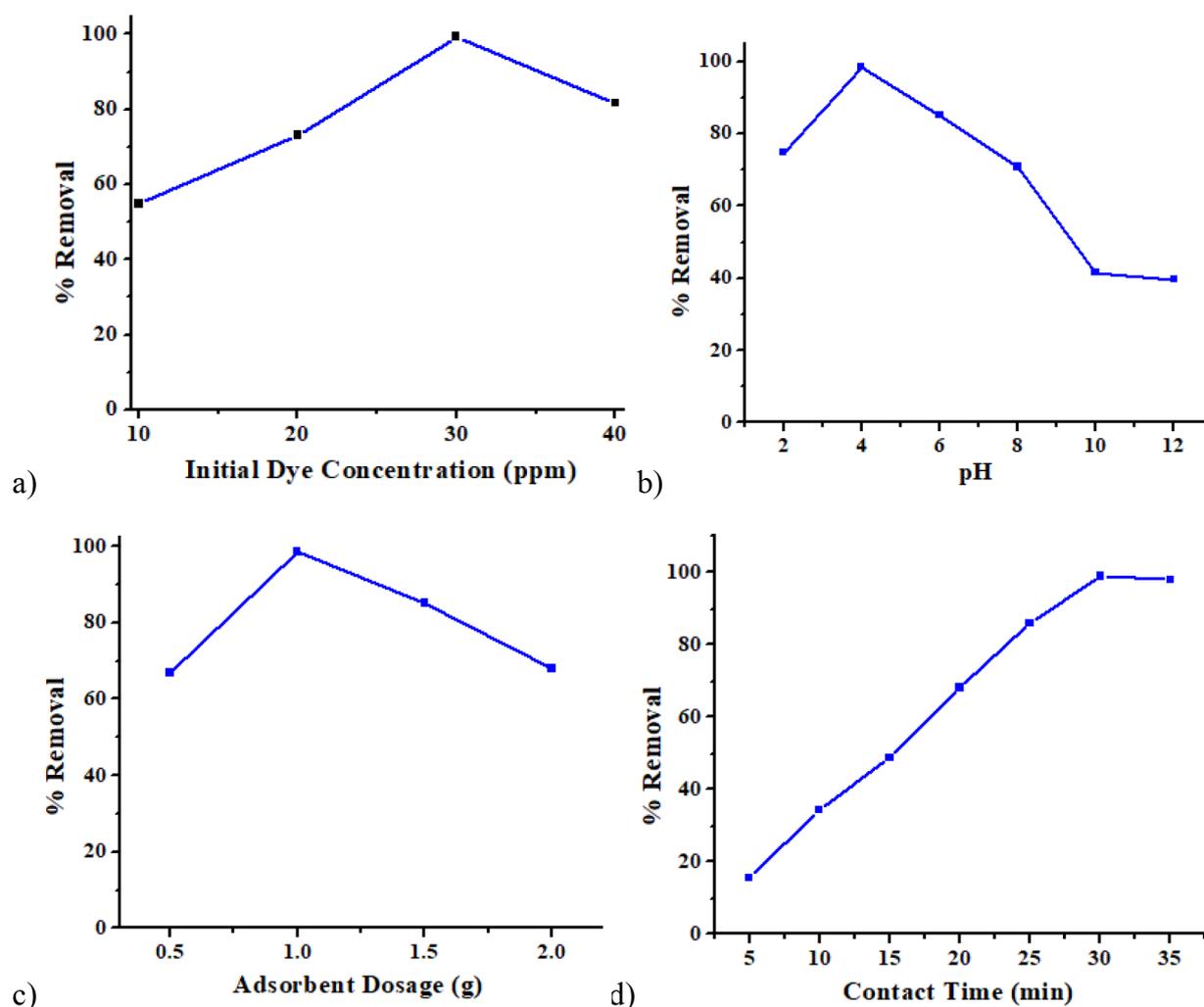Fig. 4. Effect of concentration on the removal of Chromium (VI) ions from aqueous solution.

Fig. 5. a) Effect of initial concentration of methyl-red dye, b) Effect of pH on the adsorption of methyl-red dye c) Effect of adsorbent dosage on removal of methyl-red, d) Effect of contact time on the removal of methyl-red.

the adsorbent surface) [34]. In other words, at the beginning of the process large number of easily accessible vacant sites of the adsorbent are available for adsorption, but after some time, the remaining sites are fewer and less accessible due to repulsive forces that may exist between the dyes molecules on the surface and the un-adsorbed dye molecules which resulted in decreasing the adsorption of methyl red.

3.2.2. Effect of pH

The effect of initial pH on the uptake rate of methyl-red was investigated at an initial concentration of 1 g since pH is one of the most important factors that affect the adsorption process. The efficiency of adsorption process depends on the pH of a solution as a variation in pH leads to the variation in the surface properties of the adsorbent as well as the degree of ionization. A number of experiments were carried out in the pH range of 2–12 values as indicated in Fig. 5b. The amount of dye adsorbed per unit weight of adsorbent increased till the pH values reached 4 and then started to decline beyond 4. The maximum adsorption

capacity of the methyl-red from aqueous solution occurred at pH-4 whereas minimum was achieved at pH 12. At low pH, more protons are available causing both the adsorbent surface and the adsorbate positively charged that resulted in low adsorption. However as pH increased to 4 at which the methyl red starts to be negatively charged which caused to have more electrostatic attraction between the adsorbent and the adsorbate thereby leading to maximum adsorption of methyl red. As the pH of the solution increased, the positive charge on the adsorbent surface decreased and the number of negatively charged sites increased. A negative charged surface site on the clay does not favour the adsorption of anionic dye due to electrostatic repulsion [24]. Many authors have also reported similar results [34–36].

3.2.3. Effect of clay dosage

Adsorbent dosage is also an important parameter since it determines the capacity of adsorbent for a given initial concentration of the adsorbate at the operating conditions. A series of experiments were carried out by changing the

amount of ZcAd clay from 0.5–2 g to determine the effect of ZcAd clay dosage on the adsorption of methyl-red as shown in Fig. 5c. The proportion of dye removal increased sharply from 66.9 to 98.6% when the clay dosage increased from 0.5 to 1 g (Fig. 5c). When the amount of clay increased to 1.5 g, the percentage of removal declined to 85.2%. Further increase of clay dosage decreased the removal or adsorption to 68.1%. The maximum removal or adsorption of dye was achieved at dosage of 1 g. The increase of dosage increases adsorbent sites and thus surface area of contact with the dyes increases. Therefore, the amount of dye uptake increases and consequently leads to a better adsorption. The increase in methyl red adsorption with the increase in activated clay dosage is attributed to increase in surface area of micro pores and the increase in availability of vacant adsorption sites [34]. Several scholars have also reported similar results [37,38].

3.2.4. Effect of contact time

To determine the optimal adsorption time for the dye, a series of experiments were run in the range of 1–35 min. The effect of contact time on the adsorption of methyl-red onto clay is represented in a plot of percentage adsorption versus contact time as shown in Fig. 5d. The adsorption rate was rapid in the first 30 min where a maximum removal or adsorption of the dye was achieved, leading to a methyl red removal of more than 99%. However the adsorption declined after 30 min, indicating the exhausting of the clay to adsorb more dyes and hence slower rate of removal of dye was observed. The relatively high rate of removal at the initial stage may be due the availability of large number of free adsorption sites, but after a certain time the vacant site is occupied resulting in slow adsorption rate due to slower diffusion of solute into the interior of the adsorbent [39]. Significant colour change was observed after treatment of aqueous methyl-red solution with sulfuric acid activated Zemero clay (Fig. 6).

The FT-IR spectra of natural, activated (with 25% H_2SO_4) and activated clay after adsorption of chromium (IV) and

Fig. 6. Methyl-red aqueous solution before and after treatment with 25% H_2SO_4 modified Zemaro clay mineral.

methyl red are indicated in Fig. 7. The band appeared at 3620 cm^{-1} is attributed to stretching vibration of hydroxyl groups coordinated to octahedral cations. The bands at 3420 and 1639 cm^{-1} are associated with stretching and bending vibrations respectively for the hydroxyl groups of free water molecules. The band at 1035 cm^{-1} is attributed to Si–O in-plane stretching. After acid activation of the clay, the intensity of the bands at 3420, 1639 and 3620 cm^{-1} decreased as demonstrated in Fig. 7. The decreasing in intensity of these bands is due to the removal of the cations that cause loss of water and hydroxyl groups coordinated to them [40]. The band at 795 for free silica which always present in natural samples. There are also bands at 698, 536, and 468 cm^{-1} which are due to Si-O out-of-plane bending, Si-O-Al bending and Si-O-Si in-plane bending respectively.

3.3. Adsorption isotherm

Adsorption isotherm describes the equilibrium adsorption of materials on a surface at constant temperature. The two known models namely Langmuir and Freundlich isotherms were used to investigate an interaction of dye and modified clays interaction in this study. The Langmuir model is based on the assumption that mono layer is formed on the surface of the adsorbent, and the surface is
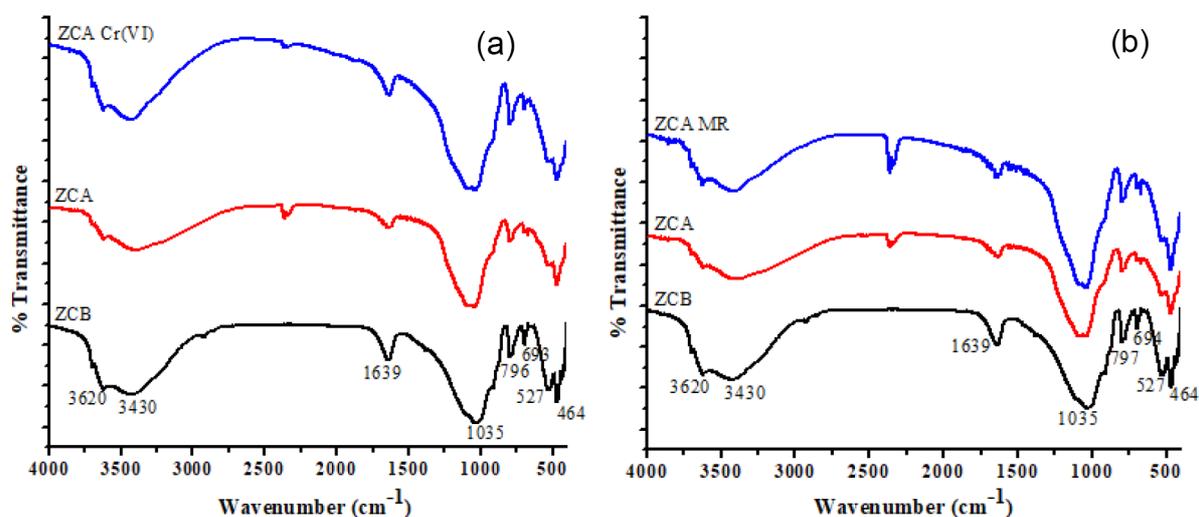

Fig. 7. FT-IR spectra of before and after activation of Zemero clay (ZCB: before activation, ZCA: after activation with 25% H_2SO_4 and after adsorption of Cr (IV) and methyl red (ZCA Cr (IV) and ZCA MR respectively).

homogeneous in character and has identical and energetically equivalent adsorption sites. Whereas the Freundlich isotherm model considers multilayer and heterogeneous surface adsorption and the exponential distribution of sites and their energies [41].

The isotherm results were carried out by containing methyl-red dye with 1 g/60 mL of adsorbent for 30 min at different initial concentrations ranging from 10 to 40 mg/L at room temperature. Fig. 7 shows the adsorption isotherms of methyl-red solution treated by sulfuric acid (25%) activated Zemero clay. The relative parameters of each isotherm was obtained according to the intercept and slope from the plots of C_e/q_e vs C_e and log q_e vs log C_e, respectively, and their correlation coefficients (R^2) from the linear isotherm model are illustrated in Table 1. The Langmuir isotherm is represented by the following linear equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m}b + \frac{C_e}{q_m} \tag{2}$$

where q_e is the amount of methyl-red adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of dye in solution (mg/L), q_m is the measurement of the adsorption capacity (mg/g) based on Langmuir isotherm and b is the Langmuir constant. From the plot of C_e/q_e vs C_e (Fig. 8a), almost a straight line was obtained with a slope value of 0.0231, q_m values of 43.29 mg/g and an intercept of 1.4972 and b value of 0.0154. The value of R_L was found to be 0.684 as indicated in Table 1, conforming the feasibility of

the adsorption isotherm in between 0 and 1 which indicates a favorable adsorption i.e. the adsorbate in solution have tendency to be adsorbed on the 25% sulfuric acid activated Zemero clay adsorbent.

The Freundlich isotherm model considers multilayer and heterogeneous surface adsorption and the exponential distribution of sites and their energies [42]. The linearized form of the equation is:

$$log\, q_e = \log K_f + \frac{1}{n}log\, C_e \tag{3}$$

where K_f (mg/g)(L/g)^n and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. As indicated in Fig. 8b, nearly straight line is obtained by plotting log q_e versus log C_e with a slope of 1.8429 and an intercept of 0.003. The value of 1/n (0.543) is between 0 and 1, and the n value (1.8429) is between 1 and 10, showing a favorable condition for sorption. Both the Langmuir's and Freundlich's plots were interpreted with respect to correlation coefficient (R^2), which is a statistical measure of how well the regression line approximates the real adsorption data Table 1. In this study, the adsorption isotherm of the activated Zemero clay adsorbent showed better fit to Langmuir than the Freundlich isotherms model (i.e. 0.976 and 0.884, respectively). Conformation of the experimental data to the Langmuir isotherm model indicates the homogeneous nature of adsorbent surface i.e. each dye molecule/adsorbent surface adsorption sites are equivalent, and there are interactions between adsorbent molecule and adjacent sites [28].
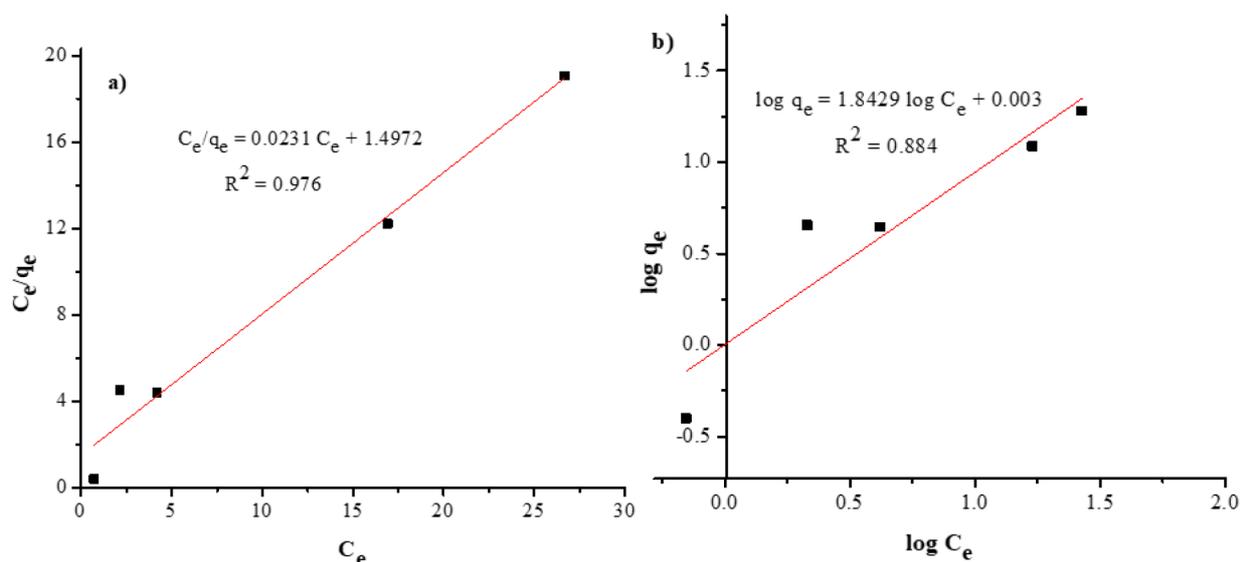

Fig. 8. Langmuir (a) and Freundlich (b) adsorption isotherm of methyl-red by activated Zemero clay adsorbent at (C_o = 30 mg/L, pH = 4.0, adsorbent dose = 1 g/60 mL, time = 30 min and at room temperature).

Table 1
Langmuir and Freundlich isotherm constants for methyl-red adsorption by activated Zemero clay

Adsorbent	Langmuir model				Freundlich model		
	q_m (mg/g)	b	R_L	R^2	K_f	$1/n$	R^2
Activated Zemero clay	43.290	0.015	0.684	0.976	0.008	0.543	0.884

3.4. Adsorption kinetics

The study of adsorption kinetics is very useful to understand the mechanisms involved as well as to design future large-scale adsorption facilities. The controlling mechanism of the adsorption process was investigated by fitting pseudo-first and second-order kinetic models to the experimental data [43]. Pseudo-first-order kinetics model is suggested for the sorption of solid/liquid systems, which can be expressed using the following equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \qquad (4)$$

where q_e and q_t are the amount of dye adsorbed on adsorbent (mg/g) at equilibrium and at time t (min), respectively, and k_1 (1/min) is the rate constant of pseudo-first order kinetics. On the other hand, pseudo-second-order kinetics model assumes that the rate-limiting step is the surface adsorption that involves chemisorption, in which concentrations of both adsorbate and adsorbent are involved. If the rate of adsorption is a second-order mechanism, the pseudo second-order chemisorption kinetic rate equation after integration is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

The kinetics studies of methyl-red dye adsorption from aqueous solution onto the activated Zemero clay are shown in Fig. 9. Adsorption kinetics describes the rate of adsorbate uptake governing the contact time of adsorption reaction.

The pseudo-second order kinetic plot for the adsorption of methyl-red onto activated Zemero clay is presented in Fig. 9b. The results showed that the adsorption process, based on the kinetic parameters and high correlation coefficient values in Table 2, followed a pseudo-second order kinetic model. Furthermore, when compared with experimental results (1.799 mg/g), the theoretical value (1.820 mg/g) for the pseudo-second order model was much more reasonable than those for the pseudo-first order model due to the experimental (1.799 mg/g) and theoretical (1.421 mg/g) adsorbed mass at equilibrium is very low. Most of the theoretical values of the pseudo-first-order model deviated from the experimental values. The pseudo-second order model provided a better correlation with the experimental data, thereby suggesting that the adsorption of methyl-red dye onto the activated Zemero clay followed the pseudo-second-order rate equation.

4. Conclusion

The clay minerals (Zemero, Seladengay, and Mehal Meda clays), which were collected from the study area, are abundantly available for free. They demonstrated high adsorption efficiencies of methyl-red and chromium metal ion from waste water, indicating their potential to be used as alternative adsorbent. Zemero clay minerals showed the highest adsorption capacity compared to the other two clays. Sulfuric acid modified Zemero clay mineral removed 96.99% of chromium (VI) ion and 99.33% of methyl-red from aqueous solution, suggesting its high potential of adsorption capacity. In general the results of
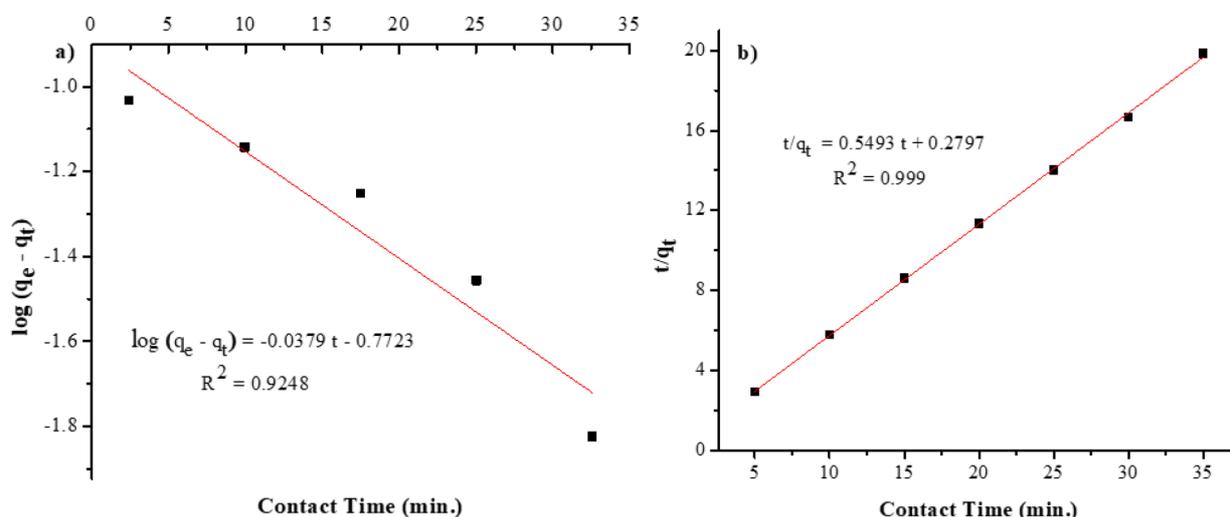

Fig. 9. Plot of pseudo-first order (a) and Pseudo-second order model (b) ($C_o = 30$ mg/L, pH = 4.0, adsorbent dose (1 g) at room temperature).

Table 2
The values of parameters and correlation coefficients of kinetic models

Experimental	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
q_e	k_1	q_e	R^2	k_2	q_e	R^2
1.799	0.077	1.421	0.925	1.079	1.820	0.999

this study show the prospect of utilizing the low-cost and locally available adsorbent for adsorption of toxic heavy metals and organic dyes effluents that can potentially pollute environment.

Conflict of Interest

The authors declare that no conflict of interest.

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