Fabrication of Novel Valorized Ecofriendly Olive Seed Residue/anthracite/chitosan Composite for Removal of Cr (Vi): Kinetics, Isotherms and Thermodynamics Modeling

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**Fabrication of novel valorized ecofriendly olive seed
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Abstract:

The present work verified the adsorption of hexavalent chromium (Cr (VI)) from synthetic aqueous solution using synthesized highly efficient low-cost adsorbent prepared from H₂O₂-modified olive seed residue solid waste/Anthracite/Chitosan (MOSR/An/CS) composite. Characteristics of the fabricated MOSR/An/CS composite were estimated by XRD, SEM, TGA, DSC, FT-IR, SBET and zeta potential tools. The entire chromium uptake study was conducted via batch adsorption mode under various operating conditions. Kinetics data were analyzed using five kinetic models, while empiric equilibrium data was fitted using three isotherms. The results clarified that Langmuir best described the adsorption of Cr (VI) ions with maximum monolayer coverage of 137.7 mg/g. Pseudo-first-order mode was nicely fitted the kinetics adsorption. Further, Elovich, intraparticle diffusion and Boyd models validates that more than one mechanism was contributed to the adsorption of Cr (VI). Besides, the estimated activation energy (E_a) and enthalpy (ΔH°) suggest the physical and endothermic nature of the adsorption process. The developed MOSR/An/Cs composite exhibited decent reusability after five sequential adsorption cycles and showed higher adsorption affinity towards Cr (VI) ions. MOSR / An / Cs composite could also be effectively used as an effective eco-friendly and recyclable sorbent for the elimination of Cr (VI) from wastewater.

Keywords: Olive stone residue, Anthracite; Chitosan; Cr (VI), Kinetics, Isotherm.

1. Introduction

Chromium (Cr) a long-standing environmental heavy metal pollutant in waste-water is generated widely by mining, electroplating, chemical manufacturing, dyeing, steel fabrication, printing, fertilizers and electronics industries. With the development of these industries, more attention was paid to the heavy metal pollutant in the water environment and the problem has become increasingly serious [Bhattacharya et al., 2019]. Cr exists in two oxidation forms i.e., (Cr (III)) and (Cr (VI)) species that have dissimilar properties. Cr(VI) has been stated to have carcinogenic and mutagenic properties [Ali et al., 2016] according to the U.S. Environmental Protection Agency (class-A carcinogen) and the International Agency for Research on Cancer (class-I carcinogen) [Goharshadi and Moghaddam 2015; Rastmanesh et al., 2018; Biglari et al., 2016]. The toxicity of Cr(VI) in humans, plants, microorganisms and animals is owing to its ability to interact with the functional bio-macro molecules in cells (i.e.; DNA) which led to structural changes [Goel, 2006]. Furthermore, Cr(VI) is about 100 times more toxic than Cr (III) due to its comparatively small size, good mobility in biological bodies, high oxidation potential and high solubility [Zhao et al., 2018]. Accordingly, it is essential to search for efficient and economical methods to treat water resources from these toxic pollutants [Ali et al., 2016].

Adsorption is the most extensively adequate technology employed for the removal of heavy metals from industrial wastewater thanks to its simplicity, easy operation, low cost and high efficiency [Bhatnagar and Sillanpää, 2017; Karamipour et al., 2019; Mondal and Chakraborty, 2020; El-Aassar et al., 2021]. Besides, the possibility of using numerous adsorbents with unique physico-chemical properties allows the potential capture of different contaminants. In the last years various effective and inexpensive natural, synthetic and modified adsorbents have been used for the reduction of Cr(VI) from aqueous systems. Biomass, industrial and agricultural wastes are amongst the materials developed for this

purpose. Some examples are seaweed bio-adsorbent [Karamipour et al., 2019], rice husk, tannin-gel [Nokano et al., 2000], wood, coconut husk and shell, lingo-cellulosic wastes, charcoal and residue of olive-mill product [Bhatnagar et al., 2014].

In the last five years, the world's olive oil production from the European Union countries reached 69 % [European Commission, 2017]. Accordingly, the approximated amounts of by-products oriented from the olive oil manufacturing compute for 6.8 million tons/year with portentous energy around 20 MJ/kg [Guizani et al., 2016 and Jeguirim et al., 2014]. A considerable magnitude of olive oil residues, such as olive husks, leaves, branches and stones are created annually, therefore, the recapture of these by-products has set off a great stump in Mediterranean countries.

Chitosan (CS) is a natural polysaccharide acquired from the Crustacean's shells (i.e., chitin) by partial deacetylation. Owes to its special characteristics such as higher OH and NH₂ concentration, non-toxicity, ease modification, bio-compatibility, bio-degradability, and eco-friendly, CS has significant potential for water treatment [Eivazzadeh-Keihana et al., 2020 and Vakiliab et al., 2019]. In order to enhance their adsorption capacity, CS has been frequently incorporated with different materials such as clay [Foroutana et al., 2020], activated carbon, carbon nanotubes [Alawady et al., 2020] and graphene oxide [Mei et al., 2020] to fabricate composites with different functionalities surface.

Herein, in this study, an innovative H₂O₂-modified olive seed residue/anthracite/chitosan (MOSR/An/CS) composite has been fabricated for the adsorptive removal of Cr(VI) from aqueous solution. The fabricated composite was characterized via different analysis tools such as FTIR, Raman laser, EDAX, DSC/TGA, SEM, EDX, X-ray diffraction, and BET surface area. The effect of initialized adsorbent concentration, adsorbent dose, temperature, pH, agitation rate, and the contact time was investigated. Further, a special

study on the isotherm, kinetics, and thermodynamics features was also reported to understand the adsorption performance of Cr(VI) using MOSR and MOSR/An/Cs composite.

2. Experimental

2.1. Materials

An olive seed residue (*OSR*) was collected from the international company for chemical fertilizer, Egypt. Anthracite (*An*) was supplied by Matrouh Water and Wastewater Company, Egypt and characterized via [El-Aassar and mohamed, 2021]. Chitosan (*CS*); purity (99.1%) and sodium chromate tetrahydrate ($\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$);purity (99.5%) laboratory-grade were supplied from Sigma- Aldrich, USA. Stock solution (1000 mg/L) of Cr(VI) was prepared by dissolving a pre-determined amount of $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ in deionized water. Acetic acid (CH_3COOH), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were supplied by Al-Naser Company for intermediate chemicals, Egypt. All chemicals employed in this study were used as received.

2.2. Preparation of chemically modified olive seed residue

A known weight of the olive seed residue (300 g) was washed with ultra-pure water, dried at 103 °C for 6 h, grounded and sieved to acquire a particle size <63 µm. In a clean glass beaker, 25 g of the obtained OSR (< 63 µm) was then treated with 25 ml of H_2O_2 under stirring for 2 h at 60 °C to obtain the H_2O_2 -modified olive seed residue (MOSR).

2.3. Preparation of modified olive seed residue/anthracite/chitosan (MOSR/An/CS) composite

Briefly, 4 g of *CS* was dissolved in 100 ml of acetic acid (3%, v/v) and stirred to attain a viscous solution of *CS*. Then, 15 ml of *CS* solution was added to 1.25 g of *An* (fine powder) and 5 g of MOSR and stirred (1000 rpm) for 4 h at 70 °C. The final solid was washed, dried at 90° C for 48 h; gently grounded and sieved below 63 µm and categorized as MOSR/An/CS composite.

2.4. Adsorbent characterization

The X-ray diffractometer using XRD (XRD-7000 with an X-ray wavelength Cu detector, Shimadzu Company, Japan) of MOSR and MOSR/An/Cs samples were performed. Morphological topographies of MOSR and MOSR/An/Cs composite were also examined using scanning electron microscopy (SEM, JEOL JSM-6610 LV, Japan). Thermal changes was evaluated using thermal gravimetric analysis (TGA-51 Shimadzu Thermogravimetric Analyzers, Japan) at a temperature range of 25-600 °C, and DSC (Shimadzu DSC-60 Plus, Japan). Further, the structural analysis was assessed using ATR-FT-IR spectrometer (Shimadzu IR–Tracer 100 Fourier Transform Infrared Spectrophotom, Shimadzu, Japan), and Raman spectra of MOSR and MOSR/An/Cs samples was determined by (HOUND UNCHAINED LABS spectrometer, Germany). The nitrogen adsorption-desorption isotherms at 77 K were measured using A NOVA 4200e (Quantachrome Instruments, USA) Surface area and pore size further analyzed using the Brunauer-Emmett - Teller (BET) equation and the specific surface area. In addition, Pore size distributions were estimated using the isothermic adsorption branch (BJH) Barrett-Joyner-Halenda technique.

2.5. Batch adsorption Experiments

The adsorption process was optimized via the batch system to define the ideal adsorption conditions of Cr(VI) onto MOSR and MOSR/An/Cs composite surfaces. In brief, different initial hexavalent Cr concentrations (10-80) mg/L (prepared by diluting the 1000 mg/L Cr(VI) stock solution) were used to investigate the effect of adsorbent dose (4-30 mg/L), agitation rate (50-250 rpm), solution pH (3-9) which adjusted with HCl and NaOH, and temperature (25-45 °C) at different residence time (0-180 min). In a typical equilibrium experiment, the fixed weight of the adsorbent (20 mg) was mixed with 50 ml of Cr(VI) solution and stirred at 200 rpm using a digital shaker (ELMI/ Europe- Model: DOS-20L) till

the equilibrium time (120 min) at constant temperature (25 °C). The adsorbate/adsorbent mixture was separated by a centrifuge (Hettich, EBA 200 S, Germany) at 10.000 rpm for 30 minutes. The residual Cr (VI) concentration was estimated by 380- 1100 nm Spectrophotometer (Model DR6000, HACH/Germany) at a wavelength of 456 nm. All the experiments were performed in triplicate and the removal efficiency (R %) and adsorption capacities (q, mg/g) were calculated as follows [Omer et al., 2020; Elzain et al., 2019]:

$$R\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q = \frac{(C_0 - C_t)V}{W} \quad (2)$$

Where, C_0 and C_t are the Cr (VI) ion concentration before and after adsorption (mg/L). V is the volume of the Cr (VI) solution (L) and W is the adsorbent mass (g).

2.6. Kinetics, isotherm and thermodynamics

To determine the adsorption path and mechanism as well as the adsorption rate, experimental data was fitted by five kinetic models namely; pseudo-first-order (Eq.3), pseudo-second-order (Eq.4), Elovich (Eq.5), intraparticle-diffusion (Eq.6) and Boyd model (Eq.7) bellowed [Khalifa et al, 2019; El-Aassar and mohamed, 2021]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = \beta \ln(\alpha \beta) + \beta \ln t \quad (5)$$

$$q_t = K_p t^{0.5} + C \quad (6)$$

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \quad (7)$$

Where, q_e and q_t (g/g) are the adsorption capacity at equilibrium and time t . K_1 (min^{-1}) and K_2 (g/g.min) are the constant rate parameters of the pseudo-first-order and the pseudo-

second-order models. β (g/g) is the number of probable active sites while α (g/g.min) is the adsorption extent. K_p (g/g.min) and C is rate constant and intercept respectively. $F = q_t/q_e$, is the adsorbed solute fraction of time t .

Adsorption isotherm [Koushkbaghi et al., 2018] was assessed using isothermal models to indicate the interaction between Cr(VI) and the synthesized MOSR/An/Cs composite. Langmuir (Eq.8), Freundlich (Eq.9) and Temkin (Eq.10) isotherm models were fitted and analyzed to describe the adsorption equilibrium data.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (8)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (9)$$

$$q_e = B_T \ln KT + B_T \ln C_e \quad (10)$$

Where, q_{max} (g/g) and K_L (L/g) are the saturated adsorption capacity and Langmuir isotherm constant. K_f is related to the adsorption capacity and $1/n$ recognized the adsorption intensity. B is the heat of adsorption (J/mol), and K_T is the maximum binding energy (L/g). Further, the adsorption favorability can be explained by R_L (dimensionless separation factor) which considered as follows [Khalifa et al., 2019; El-Aassar and Mohamed, 2021].

$$R_L = \frac{1}{1 + K_L C_o} \quad (11)$$

Thermodynamic parameters as ΔH (enthalpy), ΔS (entropy), and ΔG (free energy change) expressed by Eqs:12&13, were used to determine the direction, spontaneity and interior energy change that take place in the adsorption of Cr(VI) ion using the as-synthesised adsorbent [Jamshidifard et al 2019; El-Aassar and mohamed, 2021].

$$\ln K_D = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

Where, K_D is the thermodynamic equilibrium constant ($K_D = q_e/C_e$), ΔG and ΔH are in kJ/mol, ΔS is in J/mol.K, T is the adsorption temperature in K, and R is the universal gas constant (8.314 J/mol).

2.7. Reusability test

The reusability of the fabricated MOSR/An/Cs composite was conducted by regenerating them with 1 M HNO_3 for 6 h and the number of repeated cycles in the adsorption-desorption process was reported.

3. Results and Discussions

3.1. Characterization of OSR & MOSR/An/Cs composite

3.1.1. X-ray diffraction analysis of OSR and MOSR/An/Cs composite

The X-ray results of the raw OSR confirmed crystalline nature at 2θ equal 25° and 43° (Fig.1). Furthermore, the sharp diffraction peaks at 26° correspond to the SiO_2 reflection. [Toprak 2019; Kaklidis et al., 2014].

Fig.1. XRD pattern of OSR and MOSR/An/Cs composite.

On the other hand, the crystalline structure of MOSR/An/Cs composite was indicated by the broad peaks at 24° – 29° and 42° – 45° . The SiO_2 peaks of native OSR and MOSR/An/Cs composite is agreed with the cristobalite and tridymite peaks as a crystalline polymorph of silica which, were noticed at 20.94, 36.64, 50.17 and 60.11, 68.23 and 77.31° [Guthrie et al., 1995, Hernandez-Ortiz et al., 2015].

As illustrated in **Fig.1**; the X-ray patterns corresponding to the MOSR/An/Cs composite also confirm the same diffraction peak of OSR, but with slight shift and weaker peaks than OSR. This slight shift was caused by the decrease in the SiO_2 concentration. Further, the presence of amorphous graphite structure in the MOSR/An/Cs composite was indicated by a sharp peak at 26.5° and weak peak at 43.9° due to the random lattice structure of anthracite layers [Hernandez-Ortiz et al., 2015-Boral et al., 2015].

3.1.2. Thermogravimetric analysis/Differential scanning calorimetry analysis

Fig.2A showed the TGA analysis of the OSR and MOSR/An/Cs composite. The TGA of OSR undergoes no decomposition with loss of volatile products over the temperature range displayed from 50 and 600 $^{\circ}\text{C}$ and no considerable weight losses. Whereas the TGA graph of MOSR/An/Cs composite has a multi-stage decomposition with no stable intermediate product. Weight losses at 50 and 300 $^{\circ}\text{C}$ (1 and 2.5 percent, respectively) could be attributable to the release of volatile gases such as water vapour, CO, CO_2 , SO_2 and chitosan degradation. The thermogravimetric curve of MOSR/An/Cs composite exhibits three main decomposition steps; the initial decomposition step is due to the loss of volatile gases or adsorbed water from chitosan, whereas the second degradation step which occurred at 280–380 $^{\circ}\text{C}$ was attributed to the degradation and dehydration of the saccharide rings structure and depolymerization of the of chitosan chain [Nelson et al., 2015; Osman et al., 2003]. Besides, at 400 $^{\circ}\text{C}$ the evolution of monomeric saccharide began, and finally the third step corresponds to losses of heavy organics materials. On the other hand, **Fig.2B** illustrates the

DSC thermograms of OSR and MOSR/An/Cs composite. The figure showed that the volatile gases were lost at approximately 50°C and after this temperature the OSR reached the steady state. In contrast, volatile materials, specifically volatile gases were lost around 80 and 130°C in the MOSR/An/Cs composite owing to their high content. Besides, the thermograms shape indicates the endothermic reaction.

Fig.2. Characterization of OSR and MOSR/An/Cs composite; TGA (A), DSC (B), FTIR (C), and Raman spectra (D).

3.1.3. FTIR and Raman Spectroscopy analysis

The FTIR spectrum of OSR and MOSR/An/Cs composite (**Fig.2C**) showed the characteristic broad band's at C=C stretching, Si–O–Si, Al–O–Si and C–O bending, located at 1660, 1081, 877 and 718 cm^{-1} , respectively [Abo-El-Enein et al., 2011; Amar et al., 2020; Mohamed and Alfalous, 2020], peak at 576 cm^{-1} which ,corresponding to Fe–O [Abo-El-Enein et al., 2011] in addition to the peaks of amide group of chitosan at 1565 cm^{-1} as a weak band

[Paluszkiewicz et al., 2011 Marchessault et al., 2006], cross linking agent of C=N stretching, this observed peak confirms the strong binding of chitosan [Devi et al., 2014 and Lawrie et al., 2007]. The peak at $\sim 870\text{cm}^{-1}$ related to C-H wagging of the saccharide structure of chitosan [Darder et al., 2010; Yuan et al., 2010]. The Raman spectrum pattern of OSR is displayed in Figure 2.D, the two signals occurring about of 230 and 400 cm^{-1} are attributed to planar of 3 and 4-member ring Si-O, called D_1 and D_2 respectively. The Si-OH characteristic band is depicted round 800 cm^{-1} its intensity decreasing after of the heat treatment. Raman spectrum around 3100 cm^{-1} is assigned to the stretching modes of CH_x ($x=2, 3, 4$) [Eckmann et al., 2012]. The peaks present at 550 and 650 cm^{-1} are characteristic of the FeO groups [Zhu et al., 2010]. A Raman spectrum of the MOSR/An/Cs composite was shown in **Fig.2D**. The spectrum of (An) was attributed to the two prominent peaks G and D, Where there is a higher amplitude of the G band at 1585cm^{-1} which, indicates the appearance of the graphite structure [Inai et al., 2007; Vilarigues and Da Silva 2009 and Sadezky, et al., 2005], the increases of intensity MOSR/An/Cs composite may be due to the presence anthracite and chitosan, In the hexagonal sheet of the aromatic ring, this stage corresponds to C = C stretching. The Raman scattering mode's dual resonance assigns the Raman disorder shift at $1250\text{-}1450\text{ cm}^{-1}$, while the D-band at most represents the disorder details in lattice structures and voids in aromatic ring [Ferrari and Robertson et al., 2004; Manoj et al., 2016 and Ramya et al., 2013].

To illustrate the intensity of the shoulder peak near the D band at (1280 cm^{-1}) that may arise from the alkene-like structure stretching of C-C and C= C. In the OSR and MOSR / An / Cs composite range, the broad similarity of the broad peak position is recognized. The disorder can be determined in the MOSR / An / Cs composite graphite layer, which is in complete agreement with another announced study of graphite materials [Narandalai et al., 2016]. A signature of Raman related to chitosan appeared at 895 cm^{-1} as well as the peaks of 1587, 1420, 1377, 1346, 1262 and 1039 cm^{-1} [Ramya et al., 2013]. These feedbacks are in

conjunction with the XRD analysis obtained for the MOSR / An / Cs composite [Chen et al., 2019 and Zhang et al., 2015].

3.1.4. Surface Morphology and elemental analysis

The elemental analysis was carried out using the SEM-EDX micrograph in OSR and MOSR / An / Cs and shown in Fig.3A#& B#, respectively. Inhomogeneous topography of minerals trapped in a carbon matrix was identified by surface morphology. The EDX study showed the presence of (C, O, Na, Mg, Al, Si, Ca and Fe (C: 51.69, O: 29.48, Na: 2.01, Mg: 0.51, Al: 1.11, Si: 9.86, Ca: 3.58 and Fe: 1.75 per cent) for OSR and (C: 33.39, O: 37.93, Na: 3.85, Mg: 0.65, Al: 1.54, Si: 15.07, Ca: 5.08, S: 0.37 and Fe: 2.38 per cent) for MOSR / An / Cs as key components. The OSR and MOSR / An / C SEM diagrams are shown in Fig.3A&B. On the other hand, the incorporation of MOSR / An into Cs polymer showed bright and opaque features in MOSR / An / Cs composite. In OSR and MOSR / A / Cs composites, SiO₂ and Al₂O₃ have been identified as large particles measuring 10 µm in size. The increase in oxygen content and the decrease in carbon content of the MOSR / An / Cs composite sample may be attributed to the addition of anthracite and chitosan. Of the composite MOSR / An / Cs, there are small particles mixed on the surface of the OSR, fine lines and ultimately seen in porous form due to binding with anthracite and chitosan, as well as the action of H₂O₂ during the first stage of OSR activation. The increase in MOSR / An / Cs composite holes contributes to an increase in the surface area (103.5 m² / g), which occurred after mixing with anthracite and chitosan at temperatures of 70 and 90 ° C during the preparation and treatment of MOSR / An / Cs composites. At these temperatures, volatile gases containing CO, CO₂, and H₂ gases are evaporated, leaving these voids. [Toprak, 2019].

Fig.3. SEM images of (A, A*) OSR , and (B, B*) MOSR/An/Cs, respectively; and (A#, B#), OSR and MOSR/An/Cs elemental distribution by EDX.

3.1.5. N₂-Adsorption analysis

N₂ adsorption / desorption isotherms obtained at 77 K and BJH pore size distributions of MOSR / An / Cs composite distributions are shown in Fig.4(A, A*). The results of the MOSR / An / Cs composite based on BET analysis show the adsorption-desorption isotherms of Type I curves according to the IUPAC classification, which is an indicator of the presence of a narrow mesopore micro-porosity structure and a wider structure of micropores. The specific surface area (SSA) of the composite MOSR / An / Cs increased significantly from 10.937 m² / g to 103.292 m² / g, suggesting a high concentration of micropores in the composite MOSR / An / Cs [Cychosz, et al. , 2017], with micropores gradually rising from 0.00028 to 0.0151 (cm³ / g). Subsequently, during the preparation and curing of the MOSR / An / Cs composite, low-density volatile gases were escaped after the heat treatment of the MOSR / An / Cs

composite, suggesting a tidy formation, resulting in a shrinking hole between the layers. The pore curing will therefore extend the pore volumes and develop the SSA and the highly microporous structure of the composite MOSR / An / Cs dramatically.

In addition, the pore size distributions measured by the BJH of the composite MOSR / An / Cs are shown in Fig.4A*. As shown in the figure, the small pore diameter distribution of the composite MOSR / AN / Cs is 1.5-5 nm with large pores varying from 5 nm to more than 50 nm. As shown in the figure, the small pore diameter distribution of the composite MOSR / An / Cs in the range of 1,5-5 nm with wide pores ranging from 5 nm to more than 50 nm.

The results showed that the curing formed more pores; in the porous structure the mesoporous materials may predominate and therefore the curing results in an increase in the composite MOSR / An / Cs total surface area, which is qualitatively consistent with the modification in the (BET) surface area. The results show that the degree of microcrystalline OSR structure shifts significantly and increases the degree of graphitization due to high temperature and increased degree of carbonization, which may result in good sorptive material [Zhao et al., 2017]. However, average pore size, surface area and total pore volume obtained from MOSR/An/Cs composite derived from OSR are 30.2 Å, 103.292 m²/g and 0.0151cm³/g , respectively.

Table 1: Textural parameters of OSR and MOSR/An/Cs composite.

Specimen	SBET) (m ² / g)	Pore Size (V _t) (cm ³ / g)	The Mean Pore width (nm)
OSR	10.937	0.00028	40.3
MOSR/An/CS	103.292	0.0151	30.2

Fig.4. N₂ adsorption/desorption isotherms curves of MOSR/An/Cs composite obtained from the nitrogen gas.

3.2 Factors affecting adsorption process

3.2.1. Effect of pH

Generally, the solution pH is a vital operational parameter affecting the adsorption of heavy metals because it influences not only the surface charge of the adsorbent but also affects the metal ions speciation in the solution. **Fig. 5** depicts the impact of varying solution pH (3-9) on the adsorption of Cr(VI) ions using MOSR and MOSR/An/Cs composite. The maximum adsorption capacity of Cr(VI) onto MOSR (16.25 mg/g) and MOSR/An/Cs composite (121.25 mg/g) was observed at a pH of 3. It was worth noting that the adsorption capacity of Cr(VI) onto MOSR/An/Cs composite was higher than that of MOSR of under the same operating conditions. Depending on the solution pH different Cr(VI) species such as HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ can be present in the solution. At pH 2-6, the most prevalent Cr(VI) anionic forms are the $\text{Cr}_2\text{O}_7^{2-}$ oxyanions and HCrO_4^- which became CrO_4^{2-} with the increase in pH above 6 [Maponya et al., 2020]. At low pH (3-4), the nitrogen atoms of the amino groups (NH_2) on the surface of the composite are protonated (NH_4^+) and attract the negatively charged hexavalent chromium oxyanions, consequently, the adsorption capacity of

Cr(VI) was improved owing to the electrostatic attraction between HCrO_4^- anion (which arises from the hydrolysis of the dichromate ions as shown in Eq.14) and the positively charged composite surface (i.e., NH_4^+ , COOH_2^+ , and OH_3^+) [Bishnoi et al., 2004].

Also, the reduction of Cr(VI) to Cr(III) was attributed to the presence of electron donor-functional groups on the MMOSR/An/Cs composite surface (i.e., NH_2 and COOH) via the following reaction:

Therefore, the functional groups exist on the adsorbent surface was responsible for the removal of Cr^{6+} ions. Moreover, a simultaneous substitution reaction occurs between the adsorbent surface (positively charged groups i.e., NH_4^+ , OH_2^+ and COOH_2^+) and Cr^{3+} which improved the adsorption capacity of Cr (VI). As a result, the adsorption coupled reduction mechanism led to maximum Cr(VI) uptake at pH 3 [Vo et al., 2019 and Wu et al., 2019].

On the other hand, decreasing the adsorption capacity to 29.75 mg/g by raising the pH from 4 to 7 was due to partial deprotonation of the functional groups of the MOSR/An/Cs composite followed by the decrease of the interaction between the oxygen/amine containing-functional groups of the adsorbent and Cr (VI). Additionally, with increasing the solution pH from 8 to 10, the competition between the functional groups (i.e., OH^-) and the CrO_4^{2-} anions (the only stable oxidative form at this pH) for the active sites on the adsorbent surface was increased. Consequently, more Coulombic-repulsion anions took place [Hahid et al., 2017] resulted in a decrement of the $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} species uptake.

Fig. 5.Effect of solution pH on the adsorption of Cr(VI) by MOSR and MOSR/An/Cs composite in 50 mg/L containing Cr(VI) ion solution, adsorbent dosage 20 mg/L, contact time 120 min and 200 rpm at 25 °C.

3.2.2. Effect of initial concentration

An analysis of the sorption capacity and removal efficiency (%R) vs. initial Cr(VI) concentration was shown in **Fig. 6A**. The figure illustrates that the percentage metal ion uptake decreases from 95% to 64% with increasing the initial adsorbate concentration from 10 to 80 mg/L, while the adsorption capacity increases and reach its highest value (128 mg/g) with the raise in the Cr(VI) concentration. These results may be owing to the presence of higher energetic sites at lower Cr(VI) ion/adsorbent ratios and the large ratio of the available surface area of adsorbent to the initial number of Cr(VI) ions moles [Bishnoi et al., 2004]. On contrast, the active sits were quickly saturated by increasing the metal ion /adsorbent ratio,

thus the adsorption initiate sat lesser energy sites which resulting in a decrease in the adsorption efficiency [Mondall et al., 2020 and Goharshadi et al., 2015].

3.2.3. Effect of adsorbent dose

Fig. 6: Effect of (A) initial Cr(VI) concentration at fixed adsorbent dose of 20 mg, 200 rpm and pH=3 for 120 min at 25 °C, (B) adsorbent dose in 50 mg/L containing Cr(VI) solution 200 rpm and pH=3 for 120 min at 25 °C, (C) contact time in 50 mg/L containing Cr(VI) solution, adsorbent dose of 20 mg, 200 rpm and pH=3 at 25 °C and (D) agitation speed in 50 mg/L containing Cr(VI) solution, adsorbent dose of 20 mg and pH=3 at 25 °C on the adsorption of Cr(VI) from aqueous solution.

The influence of MOSR/An/Cs dose on the adsorption of Cr(VI) was presented in **Fig. 6B**. the adsorbent dosage increased from 4 to 20 mg, the removal of Cr(VI) increased from 20.2 to 97.4 % because the availability of more adsorptive sites for the chromium ions to adsorb [Karamipour et al., 2019]. However, additional increase in the MOSR/An/Cs

masses up to 30mg observing insignificant effect on the Cr(VI) uptake efficiency (97.8 %) due to the equilibrium between adsorbate and adsorbent at the operational conditions[Zhang et al., 2019] which known as solid-concentration-effect [Esposito et al., 2001]. On the other hand, the impact of adsorbent concentration on the adsorption capacity could be divided into two stages. When the dose of MOSR/An/Cs was raised from 4 to 12 mg, the adsorption capacity of chromium ions was sharply increased from 105.02 to 135 mg/g. Further increase in the adsorbent mass to about 16 mg, nearly keep the adsorption capacity constant (i.e., 136.25 mg/g). Oppositely, with more increasing MOSR/An/Cs dose from 20 to 30 mg, the adsorption capability would be unceasingly decreased to 81.5 mg/g.

3.2.4. Effect of contact time

The investigation of adsorption as a function of residence time (5-180 min) at initial metal ion concentration of 50 mg/L, MOSR/An/Cs dose of 20 mg and pH = 3 was described in **Fig.6C**. It was obvious that increasing contact time from 5 to 120 min improved the sorptive capacity and percent uptake of chromium significantly. The nature of sorbent and its available surface sites affected greatly the time required attaining the equilibrium. For MOSR/An/Cs this time was 120 min [Bhattacharya et al., 2008].Initially higher number of vacant active sites may be offered for adsorption but with the progress in adsorption time [Bishnoi et al., 2004], the repulsive forces between adsorbate molecules and the solid phase increased and the residual free surface sites were difficult to occupy [Saravanane et al., 2002] the adsorption affinity decreased.

3.2.5. Effect of agitation speed

Fig.6D reveals the influence of varying the agitation rate (50-250 rpm) on the Cr(VI) adsorption affinity in 50 mL containing chromium solution at pH=3 and 25 °C. It appears from the results that the uptake capacity and the adsorption efficiency of $\text{Cr}_2\text{O}_7^{2-}$, rises with an increase in the agitation speed i.e., from 11.25 to 121.87 mg/g and from 9 to 97.5%

respectively, as a result of the improvement in the solute molecules dispersion as well as increasing the exposed adsorbent surface area to the $Cr_2O_7^{2-}$ ions [Yang et al., 2019]. However, the adsorption performance reaches close constant values when the speed is 250 rpm. The plateau therefore relates to the sorption of all the available metal ions from the solution.

3.3. Adsorption kinetics and mechanism study

Table 2 clarifies the calculated parameters of the aforementioned kinetic models. The outcomes explained the q_{cal} value obtained from the pseudo-first-order model (**Fig.7A**) is very close to the value of q_{exp} compared to the pseudo-second order (**Fig.7B**). Thus, the kinetic sorption mode is best fitted by the pseudo-first order model [Itodo et al., 2010] which highlighted at the adsorption of Cr(VI) onto MOSR/An/Cs composite is favorable. Moreover, it assumes that the uptake rate of metal ions is directly proportional to the amount of available active sites on the sorbent surface [Mondal and Chakraborty, 2020]. The high initial uptake rate (h) suggesting that much chromium ions reached the sorbent surface within a short time. The probability that various forces were contributed in the adsorption of Cr(VI) from the given system, was evaluated by concerning the Elovich model (**Fig.7C**) [Khalifa et al., 2019; El-Aassar and Mohamed, 2021]. The higher value of β constant which correlated to the extension of surface coverage demonstrates that the higher surface area of MOSR/An/Cs adsorbent (**Table 2**). However, the lower value of α constant that is interrelated to the chemisorption rate suggests that the uptake of $Cr_2O_7^{2-}$ was controlled by more than one mechanism.

Fig. 7. (A) Pseudo-first order, (B) pseudo-second order and (C) Elovich kinetic models for the adsorption of Cr(VI) by MOSR/An/Cs composite.

On the other hand, the adsorption mechanism of Cr(VI) was estimated using the intraparticle diffusion and the Boyd model. **Fig.8A** clearly indicated the multiple stages for the intraparticle-diffusion model for the adsorption for Cr (VI). Further the adsorption performance was not linear over the whole time range which validating that more than one phenomenon is governing the adsorption process. The multilinear plot did not pass through the origin which proposes that the adsorption mechanism of Cr(VI) was complicated and both intra-particle diffusion (i.e., boundary-layer-diffusion) as well as surface adsorption contribute to the rate limiting step. The smaller value of Kp_1 (the slope of the first steeper stage) than the perceived value of Kp_2 (the slope of the second linear portion) also confirm this observation and agreed with other authors [Zhao et al., 2017 ; Maponya et al., 2020; El-Aassar and Mohamed, 2021]. Furthermore, the intercept values are directly proportional to the boundary layer depth as shown in **Table 2**.

454

455 **Fig.8.** (A) The intraparticle diffusion model, (B) Boyd model, (C) confirm of Boyd model.

456 Otherwise, **Fig. 8B&C** shows the linear plots of Boyd equation and its reconfirmation
 457 to differentiate between the particle and film diffusion sorption mechanism. Passing the
 458 straight line through the origin indicates that the adsorption-rate was controlled by particle-
 459 diffusion; if not, therefore it was governed by the film-diffusion. The Boyd plots clearly
 460 reveal that the controlling mechanism is film-diffusion. Related investigations were also
 461 observed by other authors [Itodo et al., 2010; Mohamed et al., 2020; El-Aassar and Mohamed
 462 2021].

463 **Table 2:** Adsorption parameters of kinetic models for the adsorption of Cr(VI) onto
 464 MOSR/An/Cs composite.

Kinetic model	Parameter	value
Pseudo-first-order	$q_{e,cal}(mg/g)$	126.51
	$q_{e,exp}(mg/g)$	122.45
	$K_1 (min^{-1})$	0.0166
	R^2	0.982
Pseudo-second-order	$q_{e,cal}(mg/g)$	193.8
	$q_{e,exp}(mg/g)$	122.45
	$K_2 (mg/g.min)$	0.00056
	$h (mol/g.min)$	2.0924
	R^2	0.914
Elovich model	$\alpha (mg/g.min)$	0.135
	$\beta (mg/g)$	34.293
	R^2	0.907
Intraparticle diffusion	C_1	2.74
	K_{P1}	7.114
	R^2_1	0.955
	C_2	38.407
	K_{P2}	14.379
	R^2_2	0.988
	C_3	117.78
	K_{P3}	0.426
	R^2_3	1

3.4. Isotherms modeling

Table 3 reports the various isotherm parameters obtained from the plotting of the four isotherm models represented in **Figs.9A-D**. The tabulated data revealed that Langmuir isotherm (**Fig. 9A**) best defined the uptake of Cr(VI) onto MOSR/An/Cs surface ($R^2= 0.994$), this suggest the monolayer adsorption with homogeneous adsorption energy [Goharshadi Moghaddam, 2015 and]. Further, the high values of q_{max} (137.7 mg/g) and low value of K_L clarifies that the synthesized MOSR/An/Cs composite has a high affinity for the selected metal ions. Furthermore, the calculated R_L value was less than 1 while the value of $1/n$ obtained from the slope of Freundlich model (**Fig.9B**) was greater than 1, demonstrating the favorable adsorption of Cr (VI). Additionally, the greater sorbent/sorbate interaction was

perceived by the higher positive value of B_T acquired from Temkin plot (**Fig. 9C**). The maximum monolayer uptake capacity of Cr(VI) in this study was compared with other adsorbents in literatures and the results were shown in **Table 4**.

Fig. 9. (A) Langmuir (C) Freundlich and (D) Temkin isotherm models for the adsorption of Cr(VI) by MOSR/An/Cs composite.

Table 3: Parameters of the different isotherm models and correlation coefficients for the adsorption of Cr(VI) onto MOSR/An/Cs composite

Langmuir				Freundlich			Temkin		
$q_{\max}$ (mg/g)	K_L (L/mg)	R^2	R_L	k_f (mg/g)	$1/n$	R^2	B_T (J/mol)	K_T (L/mg)	R^2
137.7	0.606	0.994	0.0319	0.00116	0.542	0.703	28.17	6.62	0.806

Table 4: Comparative study between the maximum adsorption capacity of Cr(VI) using MOSR/An/Cs composite and other adsorbents

Adsorbent	$q_{\max}(\text{mg/g})$	Reference
Fe ₃ O ₄ -coated CA/CS	193.2	[Karamipour, et al., 2019]
CS/Clay	80.30	[Foroutana et al., 2020]
CS/Clay/Fe ₃ O ₄	117.64	[Foroutana et al., 2020]
PVA/chitosan/A-Fe ₃ O ₄	509.7	[Koushkbaghi et al., 2017]
chitosan/PVA/zeolite	450 mg/g	[Habiba et al., 2016]
CS-Zr-GEL	138.89	[Preethi et al., 2021]
MOSR/An/Cs	137.7	This study

3.5. Thermodynamic study

The behaviour of the uptake of Cr(VI) onto the prepared MOSR/An/Cs composite was investigated using different temperatures ranged from 298 to 318 K as shown **Fig. 10A**. The results clarified that the adsorption capacity decreased from 124.375 mg/g to 114.125 mg/g with the temperature increase from 298 to 318 K, indicating that greater energy was required to overcome activation-barrier between the solid/liquid interfaces in order to allow more $\text{Cr}_2\text{O}_7^{2-}$ ions to penetrate the MOSR/An/Cs adsorbent. This decrease in the ability of adsorption may be due to a decrease in the probability of attraction between adsorbate and adsorbent, suggesting that the mechanism is exothermic.

The thermodynamic parameters explored from the slope and intercept of the plot of $\ln KD$ vs. $1/T$ given in Fig.10B can be considered for the spontaneity of the adsorption phase. The positive enthalpy value (110.11 kJ / mol), suggesting that the method of adsorption is endothermic and favorable at low temperatures, also indicated that chemisorption is Cr(VI) adsorption. This result verified that the fundamental reaction between the Cr(VI) and MOSR/An/Cs composite is at most electrostatic interactions [Khalifa et al.,2019; Ramya et al., 2013; El-Aassar and Mohamed 2021] and complex in nature (i.e., simultaneous chemical and physical reactions). Besides, the negative value of ΔS (320.75 J/mol.K) suggests randomness at the liquid/solid mediator during the adsorption of Cr(VI)

ions onto MOSR/An/Cs composite in the aqueous solution [Omer et al., 2020; El-Aassar and Mohamed 2021]. On the other hand, the positive value of ΔG varying from (14.53 to 8.1115 kJ / mol) at the temperature range measured confirms the possibility of the process as a non-spontaneous adsorption reaction. The values A (factor Arrhenius), k_{exp} (constant kinetic adsorption of Cr (VI) on MOSR/An/Cs composite and E_a (activation energy) are computed using the adsorption kinetics. In addition, the E_a value was found to be 110.11 KJ ($E_a < 40\text{kJ mol}^{-1}$ considered physicosorption, while $E_a > 40\text{kJmol}^{-1}$ defined the chemisorption process), which mean that the adsorption of Cr(VI) onto MOSR/An/Cs composite is chemisorption.

Fig. 10. (A) Effect of temperature on the adsorption process and (B) Thermodynamics of the adsorption of Cr(VI).

3.6. Adsorption mechanism

The mechanism for the adsorption of Cr(VI) onto MOSR/An/Cs composite was presented in **Scheme1**. It was noticed that the uptake mechanism of Cr(VI) mainly involves electrostatic attraction between the negatively charged Cr(VI) species and the multifunctional groups of composite such as the protonated amine groups of the chitosan and the surface complexation with carboxyl and hydroxyl groups, hence it is reduced by the adjacent electron donor groups. The Cr(VI) ions solution reduced into less toxic Cr(III) ions during the process by the attraction between the negatively charged groups (COO^-) of the MOSR/An/Cs

and chromium ions. In addition, the Cr(VI) metal ions can be adsorbed by Si-O group through ion exchange mechanism [Periyasamy et al., 2017; Mohamed, and Alfalous, 2020].

Scheme 1. Mechanism of the Cr(VI) adsorption by the MOSR/An/Cs adsorbent composite.

3.7. Evaluation of adsorbent reusability

Capability of the sorbent materials to be regenerated and recycled several times is a significant economic factor, as it governs the production cost. Herein, the chromium-adsorbed composite was regenerated to recover the instantaneous attraction between the metal ions and the adsorbent surface. **Fig. 11** verified that the as fabricated MOSR/An/Cs composite adsorbent retain a high uptake affinity, where the Cr(VI) removal (%) still exceeded 65% and after five successive cycles and. The obtained results demonstrate the aptitude of the synthesized composite as an effective and recyclable adsorbent for the Cr(VI) removal.

Fig. 11. Reusability of MOSR/An/Cs adsorbent composite.

4. Conclusion

The present study showed the suitability of the fabricated MOSR/An/Cs composite for the adsorption of Cr(VI) from aqueous solution. The developed adsorbent was well-characterized via different characterization tools. Parameters affecting the uptake of Cr(VI), including solution pH, contact time, adsorbent dose, initial metal ion concentration, agitation rate and temperature were studied and optimized. Isotherm results clarified that the adsorption of Cr(VI) onto MOSR/An/Cs is exhibited monolayer sorption with maximum adsorption capacity of 137.7 mg/g at pH 3. Additionally, the kinetics performance revealed that the pseudo-first-order model accurately fitted the adsorption process. Besides, Elovich, intraparticle diffusion, and Boyd models assumes that more than one mechanism was involved in the adsorption of chromium onto OSR/An/CS. The thermodynamic parameters

i.e., activation energy (E_a) and ΔH° suggest the major suggestive mechanism is physical, endothermic and entry driven adsorption. Furthermore, the regeneration and reusability investigations designated that MOSR/An/Cs adsorbent still reserved decent adsorption behavior even after five succeeding cycles. Therefore, the formulated MOSR/An/Cs composite could be used as an effectual and reusable sorbent for the removal of Cr(VI) from wastewater.

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Figures

Figure 1

XRD pattern of OSR and MOSR/An/Cs composite.

Figure 2

Characterization of OSR and MOSR/An/Cs composite; TGA (A), DSC (B), FTIR (C), and Raman spectra (D).

Figure 3

SEM images of (A, A*) OSR , and (B, B*) MOSR/An/CS, respectively; and (A#, B#), OSR and MOSR/An/Cs elemental distribution by EDX.

Figure 4

N₂ adsorption/desorption isotherms curves of MOSR/An/Cs composite obtained from the nitrogen gas.

Figure 5

Effect of solution pH on the adsorption of Cr(VI) by MOSR and MOSR/An/Cs

Figure 6

Effect of (A) initial Cr(VI) concentration at fixed adsorbent dose of 20 mg, 200 rpm and pH=3 for 120 min at 25 oC, (B) adsorbent dose in 50 mg/L containing Cr(VI) solution 200 rpm and pH=3 for 120 min at 25 oC, (C) contact time in 50 mg/L containing Cr(VI) solution, adsorbent dose of 20 mg, 200 rpm and pH=3 at 25 oC and (D) agitation speed in 50 mg/L containing Cr(VI) solution, adsorbent dose of 20 mg and pH=3 at 25 oC on the adsorption of Cr(VI) from aqueous solution.

Figure 7

(A) Pseudo-first order, (B) pseudo-second order and (C) Elovich kinetic models for the adsorption of Cr(VI) by MOSR/An/Cs composite.

Figure 8

(A) The intraparticle diffusion model, (B) Boyd model, (C) confirm of Boyd model.

Figure 9

(A) Langmuir (C) Freundlich and (D) Temkin isotherm models for the adsorption of Cr(VI) by MOSR/An/Cs composite.

Figure 10

(A) Effect of temperature on the adsorption process and (B) Thermodynamics of the adsorption of Cr(VI).

Figure 11

Reusability of MOSR/An/Cs adsorbent composite.

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