#### RESEARCH



# Removal of Chromium (VI) and Acid Orange 142 dye from Contaminated Wastewater using Bio-waste Mycelium of Aspergillus Ustus: Extraction, Isotherms and Kinetics Studies

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#### Abstract

This work reported the adsorption of Cr (VI) ions and acid orange 142 dye onto dead fungal biomass. The mycelium of *Aspergillus ustus (MAU)* was successfully cultured, grown, extracted and utilized as an efficient adsorbent. The extensive characterization studies of the as-prepared *MAU* sample were achieved with the Fourier Transform Infrared Spectrophotometer (FTIR), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses. Process variables' effects were conducted in the following ranges: pH (3.0–6.0), contact time (0–120 min) and *MAU* dosage (0.5–5.0 g/L). The FTIR studies revealed that the amino, hydroxyl, and acetamide functional groups on the *MAU* provided veritable sites for Cr (VI) and AO142 binding. Optimum Cr (VI) uptake was however recorded at 80 min at pH 5.0, while that of AO142 dye was established at 120 min and pH 3.0. The Temkin and pseudo-second-order model aptly described the experimental isotherm and kinetic data. Hence, the *MAU* was efficient at adsorbing Cr (VI) and AO142 dye from an aqueous solution, but with a higher adsorption capacity for the AO142 molecules.

Keywords Aspergillus ustus · Hexavalent chromium · Acid orange 142 dye · Adsorption · Fungal biomass

# Introduction

The increased anthropogenic activities and poor wastewater disposal habits have heightened the incidences of heavy metal pollution and its attendant environmental toxicity [1]. The main contributory factor to the toxicity of heavy metals in the aquatic environment lies in their high solubility and bioaccumulation tendencies [2]. Different heavy metals and dye materials constantly find their way into the aquatic environment with severe deleterious consequences. Generally, wastewater from electroplating, refineries, textile dyeing and

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leather tanning industries is heavily coloured and also laden with chromium contaminants of different valence states [3].

According to the United States, Environmental Protection Agency (USEPA), the chromium concentration benchmark in drinking water, inland surface water, marine coastal areas and public sewers are placed at 0.05, 0.1, 1.0 and 2.0 mg/L, respectively [4]. According to Asfaw et al. [5], the concentrations of total Cr, Cr(III) and Cr(VI) ranged from 1.24 - 823.87 mg/L, 1.21 - 821.86 mg/L and 0.033 - 2.01 mg/L for tannery wastewater collected from Kombolcha, South Wollo and Ethiopia, respectively. In terms of environmental stability, only the hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)] are noteworthy, but the Cr(VI) uptake is emphasized in this study as it depicts much more toxicity [6, 7]. Consumption of Cr(VI) contaminated water can be carcinogenic, mutagenic, and teratogenic to biological systems [8]. Also, increased fish mortality, as well as skin allergies, birth defects, and infertility in humans due to exposure to Cr(VI) has been reported [9, 10]. Similarly, acid orange 142 (AO142) dye as a water-soluble anionic (acid) dye is composed of benzene, nitrobenzene and other aromatic groups [11]. Due to these chemical components, acid orange 142 dye contamination has toxic and mutagenic implications for the aquatic ecosystem [12]. Cases of severe genetic mutilation and rhinitis due to the presence of AO142 dye in the aqueous environment and its subsequent ingestion has been reported [13]. Considering the aforementioned consequences of Cr(VI) and AO142 dye contamination, their efficient detoxification from the aqueous environment is paramount.

The physical and chemical techniques which have been explored for achieving efficient sequestration of both contaminants have some associated limitations [14]. For instance, the electrochemical precipitation technique which showed about 99.0% efficiency for removing Cr(VI) and colour degradation is energy-intensive [4]. Also, the sulphide precipitation approach utilizes expensive reagents and generates secondary effluents [15]. Meanwhile, the adsorption technique using microbial communities is not only efficient but also operationally flexible [16–18].

Fungi, a member of the microbial communities are preferred as potential sources of cheap biosorbent material due to their high surface area and abundant intracellular spaces which are efficient for both heavy metal and organic pollutant sequestration. Both dead and living fungi have a remarkable capacity to take up harmful contaminants from aqueous solutions. However, for a variety of reasons, dead biomass was thought to be preferable to living biomass [19]. The primary contributing factor was the large surface area of the dead cells since the majority of dyestuff binding on fungal biomass occurs via physisorption onto the two-dimensional solid cell wall. On the other hand, were not the best choice for biosorbents due to their small size and weak mechanical strength which often requires substantial hydrostatic pressure to sustain the solute flow rate. The system could be operated at various pH levels and temperatures, with no deleterious effects on the dead biomass. Additionally, using dead biomass saved money because it eliminated the need for media for fungus growth. Recycling of dead biomass is also possible after regeneration, a development which is far more difficult for live biomass. Sharma et al. [20] studied the adsorption of mercury  $(Hg^{2+})$  ions onto white rot fungus (Phlebia floridensis). The post-adsorption sample analyses revealed about 70% - 84% removal efficiency. Three fungal strains were tested for removing Thallium ions from aqueous solutions [21]. The respective fungal strains showed excellent removal performance, with maximum adsorption capacities of 94.69 mg/g, 66.97 mg/g, and 52.98 mg/g for Fusarium sp., Arthrinium sp., and Phoma sp., respectively. Also, Scopulariopsis brevicompactum [22] and Aspergillus terricola [6] were isolated and respectively explored for Pb (II) and Cr (VI) adsorption. However, optimal heavy metal uptake was achieved in both studies. Almeida and Corso [23] adsorbed acid blue 161 and procion red MX-5B dyes on the fungi Aspergillus niger, Aspergillus terreus and Rhizopus oligosporus biomasses. The fungal biomass demonstrated good adsorption capacity, with efficient toxicity elimination. This study explored the adsorptive potentials of mycelium from Aspergillus Ustus (MAU) towards aqueous AO142 dye and Cr (VI) ions in a batch system.

# **Materials and Methods**

#### Materials

The Aspergillus ustus strain was obtained from the culture collections of the Department of Microbial Chemistry, National



**Scheme 1** Presentation of the different processes involved during the adsorbent synthesis

**Table 1**The isotherm modelequations applied in the study

Isotherm models				
2-parameter models		3-parameter models		
Langmuir	$q_e = \frac{q_m k_L C_e}{1 + k_L C_e}$		Hill	$q_e = \frac{q_{mH}C_e^{n_H}}{K_H + C_e^{n_H}}$
Freundlich	$q_e = K_F (C_e)^{\frac{1}{n_F}}$		Sip	$q_e = \frac{K_s * C_e^{\beta_1}}{1 + a_s * C_e^{\beta_1}}$
Tempkin	$q_e = \frac{_{RT}}{_{b_T}}ln\big(K_TC_e\big)$		Toth	$q_{e} = rac{k_{T} * C_{e}}{\left(a_{T} + C_{e} ight)^{t^{-1}}}$
Kinetic models				
Pseudo-first-order (PFO)		$q_t = q_e [1 - exp(-k_1 t)]$		
Pseudo-second-order (PSO)		$q_t = \frac{k_2 * q_e^2 * t}{(1 + k_2 * t)}$		
Bangham		$\boldsymbol{q}_t = \boldsymbol{q}_e \big[ 1 - exp \big( -k_b t^n \big) \big]$		

 $[a_p, Toth$  isotherm constant  $(L/mg); b_p$ , Temkin constant that is related to the adsorption heat  $(J/mol); k_1$ , Pseudo-first-order rate constant  $(1/min); k_2$ , Pseudo-second-order rate constant  $(g/mg^* min); K_F$ , Freundlich isotherm constant  $[(mg/g) (L/mg)^{1/n}]; K_L$ , Langmuir constant  $(L/g); K_p$  Temkin initial adsorption rate  $(mg/(g min)); n_p$ . Freundlich adsorption intensity; R, Universal gas constant  $(8.314 J/Kmol); R_L$ , Langmuir's dimensionless constant (separation factor); T, Temperature  $(K); q_{max}$ , maximum adsorption capacity  $(mg/g); K_s$ , Sips isotherm model constant  $(L/g); \beta$ , is Sips isotherm exponent;  $a_s$ . Sips isotherm model constant  $(L/g); K_s$ . Sips isotherm model constant  $(L/g); n_H$ , Hill cooperativity coefficient of the binding interaction;  $q_{mH}$ , Hill isotherm maximum uptake saturation  $(mg/L); K_H$ , Hill isotherm constant,  $K_b$ , Bangham model constants; n, Bangham model exponent]

Research Center, Dokki, Cairo, Egypt. The following reagents used in the study: Potassium dichromate from Sigma-Aldrich (Brno, Czech Republic), sodium hydroxide, sodium carbonate, nitric acid, HCl, ethyl alcohol, and acetone were laboratorygrade chemicals (Merck, Germany).

# Preparation of Growth Medium for Mycelium Extraction

Suspend 26.5 g of PDB powder in 1 L of deionized water, then the solution was heated to 100 °C until completely dissolved. The obtained solution was sterilized at 121 °C for 15 min in an autoclave. The growth medium was studied in conical flasks containing PDB medium (50 ml). Cultures were incubated on a rotary shaker at 30 °C and 150 rpm for up to 7 days. Mycelium was removed from the media by filtration. The protocol for extracting the mycelium is detailed in our previous work [6] and schematically illustrated in Scheme 1.

#### **Batch Adsorption Studies**

The equilibrium and kinetic experimental procedures have been reported previously [24]. The experiment was conducted at the following reaction conditions: *MAU* dosage, 0.2 g/L; initial Cr (VI) and AO142 dye concentration, 10–100 mg/L; temperature, 30 °C; stirring speed, 200 rpm; contact time, 0–180 min. The Cr (VI) and AO142 dye concentrations in the supernatant solution were respectively determined by the diphenyl carbazide method [25] and on a Shimadzu UV/Visible Spectrophotometer at ~480 nm wavelength. The amount of the respective pollutants adsorbed at each instant  $(q_t, mg/g)$  and equilibrium  $(q_e, mg/g)$  is evaluated from Eqs. (1) and (2), respectively.

$$q_t = \frac{\left(C_o - C_t\right) * V}{W} \tag{1}$$

$$q_e = \frac{\left(C_o - C_e\right) * V}{W}$$
(2)

where  $C_o (mg/L)$ ,  $C_e (mg/L)$  and  $C_t (mg/L)$  are the initial, equilibrium and instantaneous adsorbate concentrations, respectively. V (L) is the volume of adsorbate solution used and W (g) is the mass of the adsorbent.

#### Mathematical and Theoretical Backgrounds of the Studied Models

The mathematical expression of the different models adopted in this study is shown in Table 1. The theoretical basis and fundamental assumptions of the respective models are briefly highlighted herein. Fundamentally, the PFO model postulates that  $\frac{dq_t}{dt} \propto (q_e - q_t)$ . Where  $\frac{dq_t}{dt}$  and  $(q_e - q_t)$ are solute uptake rate and amount of solute adsorbed at equilibrium and at any given time during the process. The PSO model assumes the vacant site occupation follows a second-order rate [26]. The Bangham model assumes an intra-diffusion [27] and thus implies the predominance of solute diffusion into adsorbent pores under conditions of uniform chemical composition [28].

The Langmuir and Freundlich equations describe solute adsorption onto homogenous and heterogenous surfaces

while the Temkin equation describes the variations in adsorption energy mostly for chemisorption [29]. The Hill, Sips and Toth models are 3-parameter isotherms based on Langmuir and Freundlich model characteristics. Specifically, the Hills model explains solute binding onto homogeneous substrates as a cooperative monolayer binding onto nonuniform sites of the same adsorbent [30]. The cooperative phenomenon implies that solute binding on one site could influence the energy and stability of the other sites on the same adsorbent. The Sip model is an upgraded form of the Freundlich model [29]. The model exhibits either Freundlich or Langmuir model characteristics based on the concentration of the adsorbate. The Toth model postulates uneven distribution of adsorption energy between the sorption sites of an adsorbent [31].

#### **Error Analysis**

The fitting goodness of nonlinear models is generally determined using specialized error models. Table 2 presents the mathematical expression of the different error models adopted in the study. Meanwhile, by applying different error models, varying error values were also generated. Hence, to ensure a holistic model analysis, these error values were normalized following the procedure we previously reported [32, 33] to generate the sum of normalized error (SNE) values.

# Instrumental and Physicochemical Characterization Procedures

The FTIR measurements were conducted on a PerkinElmer spectrophotometer within the 4000 to 400 cm<sup>-1</sup>, while the SEM and EDX results were respectively determined on a scanning electron microscope (model JEOL-JSM-5600) and

 Table 2
 Mathematical expression of the error models

Error Function	Equation	Eq. no
ARE	$\sum_{i=1}^{n} \left  rac{q_{e,exp} - q_{e,exl}}{q_{e,exp}}  ight $	(3)
APE	$\frac{\sum_{i=1}^{n} \left  \left[ (q_{e,exp} - q_{e,cal})/q_{e,exp} \right] \right }{N} * 100$	(4)
ERRSQ	$\sum_{i=1}^{n} \left[ q_{e,cal} - q_{e,exp} \right]^2$	(5)
Hybrid	$\frac{100}{n-p} \sum_{i=1}^{n} \left[ \frac{\left(q_{e,exp} - q_{e,cal}\right)^2}{q_{e,exp}} \right]$	(6)
MPSD	$100 * \sqrt{\frac{1}{n-p}\sum_{i=1}^{n} \left[\frac{(q_{e,exp}-q_{e,cal})}{q_{e,exp}} ight]^2}$	(7)
$\chi^2$	$\sum rac{\left(q_{e,exp}-q_{e,cal} ight)^2}{q_{e,exp}}$	(8)
R <sup>2</sup>	$\frac{\sum \left(q_{e,cal} - \overline{q_{e,cap}}\right)^2}{\sum \left(q_{e,cal} - \overline{q_{e,cap}}\right)^2 + \sum \left(q_{e,cap} - q_{e,cal}\right)^2}$	(9)

n = number of data points, p = number of the model parameter

EDX spectrometer (Oxford Instruments 6587 EDX detector). The XRD patterns were obtained on a PAN analytical diffractometer (X'Pert PRO) within the reading range of 2 to 80°. The point of zero charge was determined following the mass titration approach [34]. The Brunauer–Emmett–Teller (BET) surface area measurement was achieved via the nitrogen gas adsorption–desorption method on an automated Belsorp Max surface area analyzer (MicrotracBEL Corp., Japan) at an adsorption temperature of 77 K. A precise mass of the PSP sample was measured and recorded before the analyses. Likewise, the sample underwent additional degassing for 2 h at 200 °C.

# **Results and Discussions**

#### **Characterization Results**

#### Fourier Transform Infrared Spectroscopic (FTIR) Analysis

Figure 1 shows the FTIR spectra of the native *MAU* (before adsorption), as well as those after the adsorption of Cr (VI) and AO142 molecules. The raw *MAU* shows a broad peak around 3260 cm<sup>-1</sup>, a characteristic band of all polysaccharides which represents the OH and NH groups. The peak around 2933 cm<sup>-1</sup> is due to the symmetric stretching of the – CH<sub>2</sub> group of both chitin and glucan [35–37]. Also, both peaks at 1639 and 1541 cm<sup>-1</sup> are related to the free amino and amide groups in the chitin/chitosan component of the *MAU*. The single peak at 1639 cm<sup>-1</sup> is further evidence that the *MAU* contains  $\beta$ -linkage of chitin units. The sharp peak recorded around 1020 cm<sup>-1</sup> corresponds to the C–O–C of chitin and glucan parts of the *MAU* [38].

The post-adsorption spectra were mostly characterized by either positive or negative adjustments in the intensity of the peaks involved in the sorption process. For instance, the intensity of peaks assigned to the to -NH (3360 cm<sup>-1</sup>), -OH (3294 cm<sup>-1</sup>), and aliphatic C-H (2900–2800 cm<sup>-1</sup>) slightly diminished. The peak of the primary and secondary amines located between 1660 to 1500 cm<sup>-1</sup> also diminished due to the deprotonation of the Lewis basicity of –NH and -NH<sub>2</sub> by the Lewis acidic nature of Cr (VI) and N-heterocyclic nitrogen of the AO142 dye [39]. Furthermore, the intensity reduction of the C–O–C peak at 1025 cm<sup>-1</sup> confirms a successful Cr binding onto the *MAU*.

### X-ray Diffraction (XRD) Analysis

The X-ray diffraction studies reveal changes in the structural integrity of the adsorbent sample. The spectra of native *MAU* show a broad 20 peak between 15—25°. Such observation is an indication of the amorphous nature of the *MAU* (Fig. 2). The specific peaks appeared at  $2\theta = 8.9^{\circ}$  and



Fig. 1 FTIR spectra of raw MAU, and Cr(VI) loaded MAU and dye-loaded MAU

19.8°, corresponding to the 020, and 110 planes, respectively. These two representative peaks are related to chitin polymorphs. The crystallinity of the  $\beta$ -glucan component of the MAU is responsible for both miniature peaks observed at  $2\theta = 6.3^{\circ}$  and 7.5°. In both post-adsorption spectra, the relative intensity increased substantively. This is due to the incorporation of respective adsorbates onto the MAU surface via electrostatic interaction and/or further chelation with the surface functional groups, such as amino, hydroxyl, and acetamide. Small intensity peaks at  $2\theta = 44.7^{\circ}$  and  $72.7^{\circ}$  corresponding to the residual traces of proteins inherent on the MAU surface were still retained. Consequently, the absence of any significant changes in the XRD spectra pattern after adsorption suggests a physical adsorption process, where the chemical composition of the adsorbent remains unaltered after adsorption.

#### Scanning Electron Microscopy (SEM)

Figure 3(a-b) shows the SEM images of the *MAU* before and after the adsorption process. It was observed that the native (raw) *MAU* shows a rough, compact and flake-like structure with short nanofibril morphology (Fig. 3a). The nanofibril structure is attributed to the strong -OH bonding which exists within chitin and glucan components [36]. After the adsorption process (Fig. 3b), the surface of the *MAU* disbanded into a more individual nanofibril structure. The surface morphology completely changed into more distinguished flakes due to electrostatic interaction and/or chelation of the Cr(VI) cation and AO142 molecules with the surface functional groups of *MAU* (amino, hydroxyl, and acetamide). The aggregate particles marked out in a white square shape on the post-adsorption images in Fig. 3(b &c) are respectively attributed to some adsorbed chromium ions and AO142 molecules.

#### **Energy Dispersion X-ray (EDX)**

The EDX elemental distribution mapping of the raw *MAU*, Cr(VI)@*MAU* and dye-loaded *MAU* are shown in Table 3, while the mapping spectra of the Cr(VI)@*MAU* and dyeloaded *MAU* are shown in Fig. 4. By comparing the % elemental distribution and EDX spectrum of the unloaded and Cr(VI)-loaded *MAU*, obvious Cr spectra spikes are evident (Fig. 3c). Hence, a successful Cr (VI) adsorption onto the *MAU* surface is concluded. Also, a respective increase and decrease in the %wt of oxygen and carbon compared to that of the raw *MAU* suggest the involvement of oxygen and carbon-based functional groups during adsorption.

For the dye-loaded *MAU*, unlike in the case of the Cr(VI)loaded *MAU*, the %wt of oxygen and carbon atoms both decreased. Also, a relatively high %wt S and N contents, which are obvious constituents of the AO142 dye, in the dye-loaded *MAU* further suggests successful dye adsorption.

#### Surface Area Analyses

According to the findings, MAU has specific surface areas and pore sizes of 254.376 m<sup>2</sup>/g and 1.654 nm, respectively. Meanwhile, the BET surface area measurement for fairly porous (micro-, meso-, and macroporous) materials is thought to have limitations because of its false presumptions [40]. As a result, the surface area measurement technique made popular by Barrett, Joyner, and Halenda (BJH) was also looked into (Table 4). The pore radius determined in this study by the BET and BJH measurement techniques is therefore smaller than 2 nm, which is classified as micromesoporosity according to the IUPAC [41, 42].

#### Point of Zero Charge (pHpzc) Analysis

pHpzc is another property that helps in understanding the adsorption reaction mechanism of Cr(VI) onto the *MAU* surface. Generally, for an electrostatically driven adsorption process, the cation uptake occurs mostly at pH > pHzpc, whereas anion adsorption preferential occurs at pH < pHzpc. The pHzpc for the *MAU* sample was recorded at pH 6.2 as shown in Fig. 5, hence, the optimal adsorption of negatively charged chromate ions and AO142 anionic species is expected to occur at lower pH values (pH < pHpzc). Note, the terms: pH<sub>i</sub>, pH<sub>f</sub> and  $\Delta$ pH denote initial, final and change in liquid pH.

# **Adsorption Performance**

#### Effect of Solution pH

Solution pH is an important criterion during the adsorption of cationic species, especially in the case of







Fig. 3 SEM spectra of (a) native MAU (b) Cr(VI)@MAU (c) dye-loaded MAU

adsorbents with surface charges. Figures 6(a-b) show the effect of the pH adsorbate solution on the adsorption capacity of MAU. Notably, improved adsorption was observed with a slight reduction in the acidity of the adsorbate solution, from pH 3.0 to 5.0 (for Cr(VI)@MAU) and from pH 2.0 to 3.0 (for dye-loaded MAU). Regarding the Cr(VI)@MAU (Fig. 6a), at pH 3.0, the surface of MAU is quite cationic due to the protonation of the partial amino groups  $(-NH_2 \text{ converts to } -NH_3^+)$  within its chemical structure [43]. Also, the conversion of chromium ions into chromic acid ( $H_2CrO_4$ , Eq. 3) could prohibit the affinity between the Cr ions and the protonated site on the MAU. Upon the progressive reduction of the solution acidity, the adsorption capacity was increased due to improved electrostatic adsorption between chromium oxyanions  $(HCrO_4^{-} \text{ or } Cr_2O_7^{--})$  and positively charged groups of MAU like the amino and acetamide groups. Meanwhile, by increasing the pH beyond pH 5.0, the conversion of dichromate to monochromate ions (Eq. 3) is initiated, thus an adsorption capacity reduction [44].

$$4H_2CrO_4 = (pH \sim 2) 2HCrO_4 - +Cr_2O_7^{-2} + H_2O + 4H^+ = (pH > 5) 4CrO_4^{2-} + 8H^+$$
(3)

For the dye-loaded MAU (Fig. 6b), at pH 2.0—3.0, there is a sufficient electrostatic attraction between the anionic AO142 species and the MAU surface groups, hence the observed increasing adsorption capacity. A further decrease in solution acidity resulted in electrostatic repulsion due to the presence of abundant OH<sup>-</sup> ions on the MAU surface. Thus, the optimum pH

 Table 3
 Elemental compositions of the raw and loaded adsorbents

Elements	Raw MAU	Cr(VI)@MAU	Dye-loaded MAU
C (wt %)	73.38	56.19	62.62
O (wt %)	26.62	41.53	24.79
S (wt %)	-	-	4.27
Cr (wt %)	-	0.78	-
N (wt %)	-	-	8.23
K (wt %)	-	1.50	0.09



Fig. 4 EDX spectra of Cr(VI)@MAU and dye-loaded MAU

for Cr(VI) and AO142 adsorption was established at pH 5.0 and 3.0, respectively. The result further reveals that the impact of the electrostatic interaction mechanism is strongly evident in both adsorption systems.

 Table 4
 Surface area and pore properties of MAU

Parameters	BET	BJH	
Surface area (m <sup>2</sup> /g)	254.376	99.295	
Pore volume (cm <sup>3</sup> /g)	-	0.178	
Pore size (nm)	1.654	1.925	



The relationship between the dose of adsorbent (g/L) and the adsorption capacity ( $q_e$ , mg/g), as presented in Figs. 7(ab) depicts a decreased adsorption capacity with increasing adsorbent dose. For instance, at 2.0 g/L dosage, the number of *MAU* active sites increases significantly, thus leading to their progressive unsaturation at constant adsorbate concentrations. Also, the probable agglomeration and clogging of *MAU* particles at high dosages further decrease the biosorbent surface area [45] and alter the adsorbate concentration flux [46]. Similarly, observation was have been reported previously in the literature [24, 47, 48].



**Fig. 5** Plot for the determination of the *MAU* point of zero charge



#### **Effect of Contact Time**

Figures 8(a-b) show the relationship between adsorption time and adsorption capacity at specified operating conditions. At the onset of adsorption, a rapid increase in the adsorption capacities, which is due to the presence of enough vacant adsorption sites, was observed. Also, the initial rapid uptake was possible due to the phenomenon of shortened diffusion path which ensured unrestricted adsorbate access to the nanofibrils morphology of the *MAU* [12]. Consequently, an equilibrium time of 80 and 120 min was achieved during the adsorption of Cr(VI) and AO142 dye, respectively. In conclusion, it was generally



**Fig. 7** Effect of adsorbent concentration on the adsorption of (a) Cr(VI) and (b) AO142 [*Reaction conditions: (a) 50 mg/L initial conc; 0.2 g/L adsorbent conc; contact time of 2 h; T, 30 °C; pH 5.0 (for Cr(VI)) and pH 3.0 (for AO142) adsorption*]



**Fig. 8** Effect of contact time on the adsorption of (a) Cr(VI) and (b) AO142. [*Reaction conditions:* (a) 50 mg/L initial conc; 0.2 g/L adsorbent conc; T, 30 °C and pH 5.0 (for Cr(VI)) and pH 3.0 (for AO142) adsorption]

Table 5	Kinetics	model	parameters
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PFO	PSO	Bangham
Cr(VI)@MAU		
$q_{e, cal} = 22.36$	$q_{e, cal} = 16.51$	$q_{e, cal} = 16.81$
$k_1 = 1.12$	$k_2 = 0.0007$	$k_{b} = 0.02$
SNE = 2.43	SNE = 2.32	n = 0.98
		SNE = 2.50
Dye-loaded MAU		
$q_{e, cal} = 17.11$	$q_{e, cal} = 18.15$	$q_{e, cal} = 18.71$
$k_1 = 0.20$	$k_2 = 0.0023$	$k_{b} = 0.41$
SNE = 1.17	SNE = 1.13	n = 0.98
		SNE = 1.18

The bold values provided the basis for selecting the model of best fit. Thus, the small the SNE value, the better the model fit

 $q_e$ ,  $_{exp}$  = 15.24 mg/g [for Cr(VI)@MAU] and 18.33 mg/g [for Dye-loaded MAU]

observed that the *MAU* exhibited better adsorption capacity for AO142 molecules than for Cr(VI) at the same optimal process condition. Although the reason behind the observation is not clear, however, the nature of the adsorbates played a vital role.

# **Adsorption Modelling**

#### **Kinetics Studies**

Kinetic investigations are very important in any adsorption process for eventual scale-up studies. The kinetics study for Cr(VI) adsorption was investigated under the following reaction conditions: Cr(VI) conc., 10 mg/L; adsorbent conc., 0.2 g/L; pH 5.0; temperature, 30 °C. That of AO142 dye adsorption was investigated at 10 mg/L conc; 0.2 g/L adsorbent conc; pH 3.0; temperature, 30°. Consequently, the process kinetics was investigated using three classical kinetic models whose theoretical background and mathematical expressions are presented in Section "Mathematical and theoretical backgrounds of the studied models" and Table 1. The generated model parameters and the respective nonlinear plots are presented in Table 5 and Fig. 9, respectively. Taking the SNE value (refer to Section "Error analysis") as the basis, the lower the value, the better the model description. Hence, the PSO model is considered the best fit for Cr(VI) and AO142 dye adsorption. The good fitting of the PSO model signifies the possibility of chemical interaction and complexation between the Cr (VI) ions and the functional groups of the MAU. Furthermore, the q<sub>e cal</sub>-value of the respective best-fit models exhibited a close correlation to the  $q_{e, exp}$ -value. Also, the  $k_2$ -value recorded in Table 5 was relatively much lower than the k<sub>1</sub>-value for both adsorbates and thus, implies faster second-order rate sorption.

#### **Isotherm Studies**

Isotherm studies quantify the relationship between the concentration of solute/adsorbate adsorbed onto the adsorbent ( $q_e$ , mg/g) and those still retained within the bulk fluid ( $C_e$ , mg/L) at equilibrium and constant temperature. The observation of an initial steep rising curvature in Fig. 10 (biosorption isotherm curve) shows the occurrence a typical of type I (L-type) isotherm [29] for both adsorbates.

The study further applied isotherm models for the effective description of the adsorption equilibrium. Notably, respective isotherm model parameters provide some guidance on the nature of the sorption interaction and surface properties of the adsorbent. The results from the isotherm studies are presented in Table 6 and Fig. 11. Based on the magnitude of the SNE value, the Temkin model is considered the best fit for both adsorbates and suggests a chemisorption process. This conclusion is in line with those made from the kinetics studies. Regarding



Fig. 9 The kinetics plots for (a) Cr(VI) and (b) AO142 adsorption





Fig. 10 Equilibrium adsorption isotherm for Cr(VI) and AO142 adsorption

Table 6 Isotherm model

parameters

Langmuir	Temkin	Freundlich	Hill	Sips	Toth
Cr(IV) uptake					
q <sub>max</sub> =31.84	$A_{\rm T} = 2.67$	$n_{\rm F} = 1.95$	$q_{SH} = 200$	$K_{s} = 3.14$	$k_{\rm T} = 2.40$
$K_{L} = 1.12$	$b_{\rm T} = 829.76$	$K_{\rm F} = 2.57$	$n_{\rm H} = 0.46$	$\alpha_{\rm S} = -0.05$	$\alpha_{\rm T} = 0.09$
$R_{L} = 0.035$	SNE = 1.611	SNE = 1.661	$k_{\rm H} = 618.66$	$\beta_s = 0.40$	t = 2.13
SNE = 1.658			SNE = 1.85	SNE = 1.76	SNE = 1.62
AO142 uptake					
$q_{max} = 181.52$	$A_{\rm T} = 15.28$	$n_{\rm F} = 3.99$	$q_{SH} = 201$	$K_{s} = 5.87$	$k_{\rm T} = 5.96$
$K_{L} = 1.70$	$b_{\rm T} = 113.59$	$K_{\rm F} = 8.83$	$n_{\rm H} = 0.26$	$\alpha_{\rm S} = 0.0001$	$\alpha_{\mathrm{T}} = 0.009$
$R_{\rm L} = 0.15$	SNE = 1.100	SNE = 1.109	k <sub>H</sub> =33.39	$\beta_{\rm S} = 0.25$	t=1.33
SNE = 1.148			SNE = 1.105	SNE = 1.109	SNE = 1.109

The bold values provided the basis for selecting the model of best fit. Thus, the small the SNE value, the better the model fit



Fig. 11 The Isotherm model plots for  $(a)\ \text{Cr}(\text{VI})$  and  $(b)\ \text{AO142}$  adsorption

the other model parameters, the implication to the present system is summarily presented herein. The K<sub>L</sub> value of 1.12 and 1.70 L/g for Cr(VI) and AO142 uptake, respectively suggest that the adsorbent exhibit reasonable affinity for the adsorbate [49, 50]. Also, the R<sub>L</sub> value of 0.035 and 0.15 for Cr(VI) and AO142 uptake is indicative of a favourable adsorption process [51, 52]. The positive heat of adsorption  $(b_{T})$  parameter recorded for the Temkin model for both adsorbates is far greater than unity and thus an endothermic process is favoured. Based on the literature, the Sip model respectively reduces to Freundlich and Langmuir model at  $\beta_{s}$ -value equal to 1 and 0 [53]. The  $\beta_{s}$  value of 0.40 and 0.25 for Cr(VI) and AO142 uptake suggests that both systems are tending to Freundlich characteristics. The cooperative adsorption index for the Hill model  $(n_{\rm H})$ was less than unity and indicates negative cooperativity, hence, the MAU affinity for other ligands is progressively limited as the adsorption duration extends [54, 55]. The "t " parameter of the Toth model provides insight into the heterogeneity of the adsorption system. Thus, a given adsorption system is considered heterogenous at t > 1 [56]. On this basis, the present system is a heterogenous one and this conclusion corroborates the parametric indication from the Sip model.

#### **Probable Adsorption Mechanism**

The involvement of some specific functional groups and donor sites for pollutant adsorption was verified via dedicated instrumental characterization of the adsorbent. Considering the XRD spectra, no significant structural changes were recorded as the major peaks were retained. Only a relative increase in the intensity of these peaks was observed and this indicates the occurrence of a physical adsorption process. From the FTIR spectra, the peak of the primary and secondary amines located between 1660 to 1500 cm<sup>-1</sup> generally diminished due to the deprotonation of the Lewis basicity of -NH and -NH<sub>2</sub> by the Lewis acidic nature of Cr (VI) and N-heterocyclic nitrogen of the AO142 dye. This suggests a coordinate bonding between respective adsorbates and nitrogen-containing groups on the MAU. Furthermore, the nitrogen and oxygen-based functional groups were also responsible for  $n-\pi$  (electron-acceptor) interaction, another probable sorption mechanism in this study. The n- $\pi$  (electronacceptor) interaction mechanism is evidenced in the postadsorption variation in the peak intensity and wavenumber shift observed in the C-O-C and C-O stretching groups. Also, the nitrogen-/oxygen-containing groups play a prominent role during the binding of both adsorbates. Notably,



Fig. 12 Illustration of the electrostatic interaction mechanism

**Table 7** Estimated cost ofproducing 1 kg of MAU

S/N	Material	Number of units	Net price (USD)
1	Potato Dextrose Broth (PDB)	9.60 kg	30.72
2	Energy cost for drying (80 °C, 2 h)	1.00 kWh	0.83
	Net price	-	31.55
5	Other overhead costs (5% of the net cost)	-	1.58
		Total cost [net + overhead cost]	33.13

The bold values provided the basis for selecting the model of best fit. Thus, the small the SNE value, the better the model fit

the charged adsorbate species bind to the nitrogen-/oxygenbased groups on the MAU via an electrostatic interaction mechanism as shown in Fig. 12.

# **Cost Analysis for Adsorbent Production**

Adsorbent production costing is necessary for determining the economic feasibility and sustainability of an adsorption system. It is also necessary for scale-up studies. Superficially, the adsorbent production cost can be presented as an arithmetic sum of the raw material, reagent and energy costs as shown in Table 7. According to the Table, the cost of producing 1 kg of MAU is about USD 33.13. Furthermore, in terms of adsorption process efficiency, Ighalo et al. [57] noted that adsorbent cost analysis can be considered either in terms of the adsorbent cost per gram of the adsorbate removed. Consequently, the lower the adsorption cost, the better the operational and economic feasibility of the system. The substitution of the experimental adsorption capacity (see Table 5) and the cost per kg of adsorbent (see Table 7) into Eq. (4) gives the adsorption cost of 2.17 and 1.81 USD per mg/g for Cr(VI) and AO142 dye species, respectively. Thus, the use of MAU for treating AO142 dye-contaminated wastewater is economically more feasible and sustainable compared to that of Cr(VI) contaminated wastewater.

Adsorption cost = 
$$\frac{\text{Cost per kg of adsorbent (EGP)}}{\text{Adsorption capacity of adsorbent } \left(\frac{\text{mg}}{g}\right)}$$
(4)

#### **Environmental Implications**

Following every successful adsorption cycle, the adsorbent gets solely saturated such that its adsorption capacity is completely lost with time. However, based on the principles of green Engineering, such exhausted adsorbent should be regenerated and reused. To ensure an efficient adsorbent regeneration, the choice of eluents is paramount and to make an informed choice of eluent, the nature of the adsorbent and the predominant sorption mechanism should be considered. In addition to being effective, a choice eluent should also be cheaply available, non-destructive to the adsorbent and ecofriendly [58].

The Cr(VI) adsorbed to the MAU biomass can be readily regenerated using cheaply available and eco-friendly dilute minerals and organic acids [59]. Using dilute sodium hydroxide and hydrochloric acid solutions, O'mahony et al. [60] demonstrated successful desorption of nickel, copper, zinc and cadmium cations from Penicillium biomass. However, the success of an alkaline and acid solution in desorbing heavy metal depends on the adsorbent surface charge and charge on the pollutant species [61, 62]. Furthermore, regarding the desorption of the anionic AO142 dye species, a dilute alkaline solution is used as an eluent. Consequent upon impregnation in a dilute alkaline solution (eluent), the MAU surface becomes deprotonated. Thus, the anionic AO142 dye species which were mostly bound electrostatically to the adsorbent surface would be readily dislodged via an electrostatic repulsion mechanism. This approach was successfully applied for the desorption of reactive yellow 2 dye from Corynebacterium glutamicum waste biomass [63].

After several adsorption-desorption cycles, the adsorption capacity of the adsorbent gets ultimately exhausted. However, handling these exhausted adsorbents and the solute-laden eluent solutions pose a challenge which must be cooperatively addressed to avoid creating more complex scenarios. To mitigate the aforementioned post-desorption challenges, the exhausted adsorbent can be safely disposed of using an appropriate approach, while the solute (especially heavy metals) can be recovered from the saturated eluent via either metal precipitation, or electrowinning [61, 64]. The Cr(VI) can also be transformed into a less toxic form via an oxidation-reduction reaction. Due to the minimal toxicity of the AO142 dye species used in this study, the spent MAU could be safely dumped in dedicated landfills after proper and effective desorption of the adsorbed dye [65]. The process of landfilling has the advantage of cost-effectiveness and flexibility.

#### Adsorbent Performance Comparison

The adsorptive performance of a given adsorbent is often expressed as a function of the amount of solute adsorbed

Table 8	Comparison of	the adsorptive	performance of	of different	adsorbents in	terms of the qmax	values
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Adsorbent	Adsorbate	Process variable				q <sub>max</sub> (mg/g)	Ref
		pН	Time (min)	Adsorbent dose (g/L)	Initial conc		
Mixed A. niger and A. flavus	Reactive green 6 dye	5.0	50.0	2.5	25	21.20	[67]
Mixed A. niger and A. flavus	Cu <sup>2+</sup>	5.0	50.0	2.5	25	24.92	[67]
Aspergillus Ustus	Cr(VI)	5.0	80.0	0.5	50	31.84	Present Study
Aspergillus campestris	Cu <sup>2+</sup>	6.0	30.0	1.0	50	62.02	[68]
Penicillium sp.	Ni <sup>2+</sup>	5.5	140.0	7.5	639	63.60	[69]
Trichoderma harzianum	Reactive Red-3 dye	4.0	150.0	0.5	100	172.63	[70]
Aspergillus Ustus	Acid Orange 142 dye	3.0	120.0	0.2	50	181.52	Present study
Mixed A. fumigatus and A. niger	Cr(VI)	2.0	60.0	0.7	500	249.90	[71]

The bold values provided the basis for selecting the model of best fit. Thus, the small the SNE value, the better the model fit

per unit mass of the adsorbent. Igwegbe et al. [66] reported that the rating of adsorption performance based on the %removal efficiency does not accurately reflect how well the adsorbent performs since it is heavily reliant on the initial adsorbate concentration and adsorbent dosage. Conversely, the adsorption capacity (mg/g) shows the inherent adsorption capacity of the different adsorbents. Table 8 presents the adsorption performance of different fungalbased adsorbents for adsorbing selected heavy metals and dye molecules, in ascending order of their respective q<sub>max</sub> (mg/g). Due to the surface charge of the fungal biomass, it was observed that the optimum uptake occurred within the acidic pH ranges, irrespective of the adsorbate type. Consequently, the adsorption capacities reported in the present study are well within existing values obtainable in the literature.

# Conclusion

In this research, the mycelium of Aspergillus ustus (MAU) was successfully isolated and further applied as an efficient adsorbent for the adsorption of Cr (VI) ions and acid orange 142 (AO142) dye. The pre and post-adsorption characteristics of the MAU were evaluated by FTIR, XRD, SEM, and EDX analyses. The presence of the functional groups relevant for adsorbing the respective pollutants was confirmed from the FTIR analysis. Similarly, the XRD and SEM analyses elucidated the structural and morphological properties of the MAU, while the EDX analysis confirms the Cr and AO142 dye adsorption. At optimum process conditions. it was generally observed that the MAU exhibited better adsorption capacity for AO142 molecules than for Cr(VI) at the same conditions. Although the reason behind the observation is not clear, however, the nature of the adsorbates played a vital role.

Authors' Contributions • L.A. Mohamed: Experimentation, Formal analyses, Data curation.

• Chukwunonso O. Aniagor: Conceptualization, Data curation, Supervision, Writing – Original draft, Writing – Review and editing.

• A.A. Aly: Experimentation, Formal analyses, Data curation.

• A. Hashem: Project administration, Data curation, Supervision, Writing – Review and editing.

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**Data Availability** All data generated or analyzed during this study are included in this published article.

#### **Declarations**

**Competing Interests** The authors declare no competing interests.

Ethical Approval Not applicable.

**Conflict of Interest** The authors declare that there are no conflicts of interest and there exist *no relationships or activities that could appear to have influenced the submitted work.* 

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