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25 Comparison study of biosorption and coagulation/air flotation methods for chromium

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33 Abstract

34 This work aims to compare a biosorption method (BM) and a coagulation-dissolved air 35 flotation method (C/DAFM) as inexpensive and effective means of eliminating hexavalent chromium (Cr[VI]) from industrial wastewater. Synthetic wastewater containing 1000 mg L^{-1} 36 37 chromium was used for the experiments. The effect of different parameters (initial pH, 38 amount of adsorbent, and contact time) was investigated for the BM. At optimal conditions (initial pH 3, 7 g adsorbent, and contact time 120 min) maximum Cr(VI) removal was 39 40 estimated to reach 68.1%. For the C/DAFM, poly aluminum chloride (PAC), and FeCl₃ were 41 used as coagulants and the dose was determined by jar test. In optimal conditions of pH 7.5, 42 pressure of 3 bars, and flotation time of 5 min, a maximum of 85% of chromium was 43 extracted. In a comparison of C/DAFM and BM, C/DAFM showed higher ability and greater potential for Cr(VI) removal. Process optimization was carried out using an artificial neural 44 45 network (ANN) to predict the most favorable conditions of operation for maximum 46 percentage of Cr(VI) removal from wastewater.

47 Keywords: Removal, biosorption method, coagulation–dissolved air flotation method,
48 optimization, artificial neural network.

49 **1. Introduction**

A toxic metal, Cr(VI) enters the environment through such industrial processes as 50 electroplating, chromate preparation, and leather tanning ^{1, 2}. One approach to treatment of 51 Cr(VI)-laden wastewater is reduction of Cr(VI) to Cr(III) to form a solid hydroxide¹. Ion 52 exchange ³, solvent extraction ⁴, reduction ⁵, electrochemical precipitation ⁶, and adsorption⁷⁻ 53 10 54 may also be utilized for Cr(VI) reduction, but such treatment methods present disadvantages such as high cost involved with initial investment in equipment, as well as 55 operational costs and costs for disposal of the residual metal sludge ^{11, 12}. The pursuit of 56 efficacious vet cost-effective means of Cr(VI) removal is called for. Contemporary research 57 58 has focused on biomasses derived from algae, fungi, or yeast, with a view toward the various advantages of each, including cost effectiveness, high selectivity, and eco-friendliness¹³. 59 60 Brown algae, which form a diverse class of organisms found mainly in temperate to subpolar intertidal areas of the marine environment, have shown promise in a number of investigations 61 ¹⁴. Sargassum bevanom, for example, is a species of brown algae that has a superior metal-62 63 adsorption capacity as compared to other biosorbents due to the powerful functional groups on its surface ¹⁵. 64

The technology offered by the C/DAFM has potential for removal of heavy metals and other 65 66 particulate matter from wastewater and offers a simple and cost-effective method for Cr(VI) 67 removal. Once adequate flocculation of the particles in the solution to be treated has been 68 achieved, the C/DAFM makes use of solid/liquid separation by attaching microscopic air bubbles to flocs suspended in an aqueous solution and floating the particles to the surface, 69 70 where they can be skimmed off. The bubbles are formed by a reduction of pressure in a water stream saturated with air at higher than 3 bars ¹⁶. Air introduced at the bottom of the container 71 72 of water being treated forms small bubbles that collect on the suspended matter, and float it to the surface. The particulate matter may then be skimmed from the surface. Through this 73 means particles having a higher density than the aqueous solution suspending them can be 74

75 made to float. The removed particles can be further processed, and any residuals in the treated water may be filtered out ¹⁷. Process variables that control the C/DAFM, including the 76 77 saturation pressure, air-to-solids ratio, and the hydraulic surface-loading rate, depend on the properties of the wastewater and can be adjusted to meet specific effluent quality standards ¹⁸. 78 The primary purpose of this study was to compare the effectiveness of two environmentally 79 80 friendly technologies characterized by their ability to remove heavy metals from solutions 81 without introducing pollution into the environment, as specifically applied to eliminating Cr(VI) from wastewater. Removal of chromium from wastewater using C/DAFM in 82 83 comparison with BM has not been studied previously. In this study the BM was used to 84 evaluate the potential of the brown alga S. bevanom as an adsorbent. Various factors were 85 varied for each method and their effects observed; based on this, optimal conditions for both 86 methods were established. The two methods were then compared to determine their relative 87 effectiveness under optimal conditions.

88 2. Materials and methods

89 **2.1.** Materials

90 Potassium dichromate ($K_2Cr_2O_7$) was dissolved in distilled water to make a 91 stock solution of Cr(VI) (1000 mg L⁻¹). Distilled water was added to dilute the solution as 92 needed for each experiment. HCl (1 M) and NaOH (1 M) were used to adjust the pH as called 93 for.

94 **2.2. BM study**

95 2.2.1. Biomass preparation

In the BM study, *S. bevanom* collected along the Persian Gulf, Bushehr, Iran, was used as the biosorbent in all experiments. To obtain a clean biomass, the alga was initially washed three times with deionized water. Next, the biosorbent was placed in an oven to dry for 24 h at 70 °C. The dried biosorbent was ground and then sifted to obtain a mesh size of 200–300.

100 **2.2.2. Batch experiment**

All experiments were performed using 250-mL Erlenmeyer flasks kept at room temperature and agitated occasionally at 300 rpm. Various parameters, including initial pH, adsorbent dosage, and contact time, were evaluated in the batch experiments. Also, in this study, the changing of initial pH, adsorbent dosage and contact time is from 2 to 8, from 1 to 10 g and from 15 to 150 min, respectively.

106 **2.2.3. Continuous experiments**

107 A glass column with an ID of 2 cm and 25 cm in length was used to carry out the continuous-108 flow sorption experiments. The column was fitted with an adjustable plunger and 0.5-mm 109 stainless sieves at the base and head. The bottom 2 cm of the column were filled with a layer 110 of 1.5-mm glass spheres in order to achieve a uniform intake of solution. S. bevanom was 111 placed on top of the glass beads at the selected sorbent bed height. The flow rate of the 112 Cr(VI) solution was regulated by a Miclins PP 40 peristaltic pump and forced up through the 113 column at 5 mL/min. Sampling was done from the outlet flow at designated intervals of time 114 and analyzed for presence of Cr(VI). After elution, the bed was rinsed using distilled water 115 until the wash-effluent pH had stabilized near 7. It should be noted that, at each stage, 200 ml 116 samples were taken. A diagram of the BM system used is shown in Figure 1a.

117 **2.3.** C/DAFM study

A diagram of the C/DAFM system used is shown in Figure 1b. The C/DAFM was carried out in six stages: (1) a sample solution at the desired pH was placed in the flotation tank, (2) PAC was added as a coagulant, (3) the chromium solution and PAC were mixed rapidly, (4) compressed air was injected into the flotation tank using a compressor, (5) flotation was continued for 30 min, and (6) samples were collected from the sampling point.

123 **2.4. Analytical methods**

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Analysis of the concentration of Cr(VI) in the samples was carried out using a Unicam 929 atomic absorption spectrometer (AAS). The following equation was used to calculate the removal percentage:

127 Removal efficiency % =
$$\frac{(C_2 - C_f)}{C_0} \times 100$$
 (1)

where C_0 is the initial chromium concentration (mg/L) and C_f is the final chromium concentration (mg/L).

130 The sorption capacity was computed as follows:

131
$$q_t(mg/g) = (C_t - C_t)(mg/L) \times \frac{V(L)}{m(g)}$$
 (2)

- where q is the amount of metal adsorbed at time t, C_i was the liquid-phase concentration of the solute at the initial time, C_t was the liquid-phase concentration of the solute at a given time, V was the solution volume, and m was the mass of the adsorbent.
- 135 The amount of adsorption at equilibrium was computed as follows:

136
$$q_{\varphi}(\mathbf{mg/g}) = (C_t - C_{\varphi}) (\mathbf{mg/L}) \times \frac{V(L)}{m(g)}$$
(3)

where q_e is the amount of adsorption at equilibrium and C_e is the ion concentration (mg/L) at equilibrium.

139 **2.5.** ANN process

An ANN is a system that employs numerous elements to form a computational model. The elements, or neurons, are interconnected by weight coefficients that can be used for training the ANN to solve a particular problem in a set. In most ANN systems the neurons are separated into layers, with each layer performing a specific function. The network architecture of a given ANN consists of the configuration of the layers and the patterns

145 among them. In general, the neurons within a given layer will either be connected or not. In a 146 feedforward neural network architecture, neurons connect to an output layer through an input signal. The weighted connections among neurons are adjusted using backpropagation, the 147 148 error between the input data and the predicted values is minimized using Widrow-Hoff learning ¹⁹. As ANN architecture is founded on neurons, transfer functions, layers, and their 149 150 connections, designing a specific ANN consists of configuring the number of neurons, their 151 arrangement layers, the number of layers, how the layers interconnect, the input weights, and 152 the transfer functions. Trial and error is used to establish the number of layers and the number 153 of neurons in each layer. This investigation focused on pH, amount of adsorbent, and contact 154 time as the input variables for the first network, whereas pressure, flotation time, and bed 155 height were the input variables for the second network. The experimental values for 156 percentages of chromium removal with BM and C/DAFM were introduced as network output variables (network response). MATLAB software was used ²⁰. 157

158 **3. Results and discussion**

159 **3.1.** ANN

Network training was used to determine the ANN weights. In much the same way as a 160 161 mathematical model is calibrated, 75% of the data were used for data-collection training to 162 establish the percentage of chromium eliminated from wastewater. For both the BM and the 163 C/DAFM, 20 data sets comprised the training data. Figures 2a and 2b contrast the experimental data against the values predicted by the models. The R^2 values obtained indicate 164 165 the models to be acceptable. The optimal number of neurons in the hidden layer was found to 166 be 9 neurons for both the BM and the C/DAFM (Tables 1 and 2). The root-mean-square 167 errors for the training algorithms tested are presented in Table 3. The Levenberg-Marquardt 168 (LM) algorithm was found to work best, and the LM-trained network chosen as the best 169 predictor of process effectiveness.

170 In this study, typology of chromium based on reduction of Cr^{6+} to Cr^{3+} in acidic media with

171 low pH was occurred. $2\text{HCrO}^- + 6\text{I}^- + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 8\text{H}_2\text{O}$.

I72 Iodide ion was used as a reducing agent to react with chromium (VI) and produce I^{3-} and I73 Cr(III) ions. Due to low concentration of chromium in the sample, cloud point method was used for pre-concentration to I^{-} will react with cetyl trimethyl ammonium bromide and forms a negatively charged complex. Ammonium cerium sulfate (IV) [Ce(NH₄)₄(SO₄)₄] are used to i76 oxidization of all Cr(III) to Cr(VI) and following reaction occurred: $3Ce^{4+} + Cr^{3+} \rightarrow Cr^{-6+} + Ce^{3+21}$.

178 Cr^{6+} sample was passed through the column that coated with strong acidic resin and samples 179 from its bottom collected and then preconcentration and extraction with UV-Vis device 180 carried out and finally, absorption of Cr(VI) occurred.

181 **3.2. BM result**

182 **3.2.1. Initial pH**

183 Usually pH is the most important factor in effectiveness of adsorption processes. The effect of initial pH was observed when varied from 2 to 8 at the initial chromium concentration of 184 1000 mg L^{-1} , amount of adsorbent 7 g and amount of adsorbent 10 g, and contact time of 150 185 min (Figure 2c). Above pH 3, chromium removal decreased when pH was increased. The 186 187 maximum removal obtained was 70% at pH 3. Therefore, S. bevanom was the most stable in acidic or alkaline pH conditions. The greater sorption capacity at lower pH is possibly due to 188 the breaking up of functional sites on the sorbent. In the higher pH ranges, where the 189 chromium primarily takes the form of HCrO₄⁻, removal decreased exponentially as pH 190 191 increased, due to the greater attraction between the $HCrO_4^-$ ions and the H^+ ions on the algal surface. Equilibrium for various chromium ions is shown below ^{14, 22}: 192

$$193 \quad \text{H}_2\text{CrO}_4 \leftrightarrow \text{H}^+ + \text{HCrO}_4^- \tag{4}$$

194
$$\operatorname{HCrO}_{4}^{2-} \leftrightarrow \operatorname{H}^{+} + \operatorname{CrO}_{4}^{2-}$$
 (5)

$$195 \quad 2\text{HCrO}_4^- \leftrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \tag{6}$$

196 For discussion at low pH,

Adsorption of Cr6+ below pH 3.0 suggests that bind of the negatively charged chromium 197 198 species occurred through electrostatic attraction to the positively charged functional groups 199 on the surface of sorbent cell wall due to the presence of more functional groups carrying 200 positive charge at pH < 3. While at pH > 3 the sorbent cell wall possesses more group 201 carrying net negative charge which repulses the metal anions. However, there is a removal at 202 pH > 3.0 but the rate of removal was reduced, which could be considered the presence of physical adsorption on the surface of the sorbent ²³. At low pH, on the other hand, Cr (VI) 203 had a higher redox potential and favored Cr (VI) bioreduction ^{24, 25}. Acidic pH biomass 204 205 contains the positive oxidation state of chromium due to protonation and Chromium remains in the anionic form (i.e. $HCrO^{4-}$ or $Cr_2O_7^{2-}$), hence sorbed optimally onto the active sites of 206 207 the biomass.

208 **3.2.2.** Contact time

Effect of contact time on chromium sorption by *S. bevanom* (initial pH = 3, initial chromium concentration 1000 mg/L, 7 g adsorbent) is shown in Figure 2a. Chromium sorption rate reached a maximum of 65.97% with a contact time of 120 min, with little variation in the sorption rate thereafter. Based on this observation, a 120-min contact time was used in subsequent experiments.

214 **3.2.3.** Amount of adsorbent

The effects of *S. bevanom* doses between 1 g and 10 g (in 500 mL aqueous solution, pH = 3, contact time 120 min, initial chromium ion concentration 1000 mg/L) were compared. The maximum percentage of chromium ions adsorbed was yielded with an adsorbent dose of 7 g.

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As the adsorbent dose increased from 1 to 7 g, the percentage of chromium ions adsorbed increased from 6.82% to 65.82%. Doses above 7 g did not result in any significant increase in removal of chromium. As can be seen in Figure 2b, increase in adsorbent concentration resulted in a marked increase in the adsorption percentage of chromium onto the biosorbent, which can be attributed to that fact that the increased amount of adsorbent provides greater surface area. Based on these observations, a concentration of 7 g of *S. bevanom* in the 500mL solution was chosen as an optimal amount of adsorbent.

225 Globally, it would be of relevance increasing the knowledge on Cr(VI) retention processes when this pollutant interacts with sorbent materials. In this way, Fernández-Pazos et al.²⁶ 226 227 studied quantitative and kinetic aspects regarding Cr(VI) adsorption/desorption on various 228 solid media (fine and coarse mussel shell, un-amended and mussel shell-amended forest and 229 vineyard soils, slate processing fines and pyritic material). In addition to the kinetic 230 characterization, it would be interesting to elucidate complementary aspects, such as the 231 effects on Cr(VI) retention caused by changing pH, or the fractions where the retained Cr(VI) 232 was bound, which can aid to estimate the degree of stability of that retention.

233 **3.2.4.** Cr(VI) adsorption/desorption as a function of pH

234 To study adsorption, triplicate samples (1 g) of mussel shell were added with 10 mL of solutions containing 5 mg L⁻¹ Cr(VI) and different concentrations of HNO₃ (0.0025 M, 235 0.0038 M, 0.005 M, 0.0075 M) or NaOH (0.0025 M, 0.0038 M, 0.005 M, 0.0075 M), also 236 237 including NaNO₃ 0.01M. Control samples were constituted by each of the solid materials added with 10 mL of solutions containing NaNO₃ 0.01M and 5 mg L⁻¹ Cr(VI), but without 238 239 HNO₃ or NaOH. After shaking for 24 h, all samples were centrifuged for 15 min at 4000 rpm, 240 and filtered through acid-washed paper. The resulting liquid was analyzed for pH and Cr(VI). 241 Adsorbed Cr(VI) was calculated as the difference between added Cr(VI) concentration and 242 that remaining in the equilibrium solution. Desorption was studied using triplicate samples (1)

10

g each) of the same solid materials than in the adsorption trials, that were added with 10 mL 243 of solutions containing 100 mg L⁻¹ Cr(VI), also including NaNO3 0.01M as background 244 245 electrolyte. After shaking for 24 h, all samples were centrifuged for 15 min at 4000 rpm, and 246 filtered through acid-washed paper, discarding 24 the liquid phase. The remaining solid phase 247 was then subjected to a desorption procedure, adding 30 mL of solutions containing NaNO₃ 248 0.01 M and diverse HNO3 or NaOH concentrations aiming to provide a wide pH range, then 249 being different for the various solid samples. After shaking for 24 h, all samples were 250 centrifuged for 15 min at 4000 rpm, and filtered through acid-washed paper. The resulting 251 liquid was analyzed for pH and Cr(VI). Desorbed Cr(VI) was calculated as the difference 252 between the amount retained in the adsorption phase and that released to the equilibrium 253 solution in the desorption phase, and it was expressed as percentage of the total amount adsorbed ²⁷. 254

255 **3.2.5. Bed height**

Figure 3a shows how bed heights of 10 cm, 15 cm, and 20 cm with initial Cr(VI) 256 257 concentration of 1000 mg/L and flow rate of 5 mL/min affected chromium removal. When 258 bed height was increased from 10 cm to 20 cm, the volume of the treated solution increased 259 due to increasing diffusion of the chromium ions into the sorbent, correlated to decreasing 260 axial dispersion in the mass transfer. This allowed sufficient time for the solute to diffuse into 261 the biosorbent, remaining in the column for a longer period of time and treating a greater 262 quantity of effluent. The increased sorption capacity achieved with increased bed height is 263 attributable to the greater adsorbent concentration in larger beds. With more sorption sites 264 available, the uptake of chromium ions in the column increased. The greatest Cr(VI) removal 265 (85.09%) was achieved with the maximum bed height of 20 cm. It should be noted that as the

bed height increased from 10 to 20 cm the breakthrough time also increased. Also, it shouldbe noted that, the range of 10 to 20 cm is range for sampling.

268 **3.3.** C/DAFM system

In C/DAFM systems, the liquid to be treated is first placed in a container and pressurized by dissolving air in it at approximately 1.5–3 bars. The supersaturated solution is conducted into a flotation tank, allowing the pressure to be released. Air precipitates out of the solution, forming small 30–120 mm gas bubbles, which cling to the particulate matter in the solution and raise it to the surface, allowing it to be eliminated. In this investigation, the effects of flotation time, pressure, and bed height on the C/DAFM system were investigated.

275 **3.3.1. Flotation time and pressure**

The effect of varying pressures from 1.5 to 3 bars on the chromium removal percentage at a constant flotation time of 1–6 min and bed height of 1 m in the presence of PAC as a coagulant were measured (Figure 4b). The removal of Cr(VI) increased over the first 5 min, gradually leveling off until it reached equilibrium. The chromium removal reached 85% at a constant pressure of 3 bars.

The effects of pressure are dependent on the solubility of gases in liquids. At higher pressures, more gas is soluble in any given liquid than at lower pressures; the extra gas dissolved at higher pressure evaporates from the solution when the pressure is reduced. In this study maximum chromium removal was obtained at a pressure of 3 bars, and therefore this pressure was selected as the optimal value in the following experiments.

286 **3.3.2. Bed height**

Two different bed heights, 1 m and 2 m, at a constant pressure of 3 bars and flotation time 5
min, were tested. The amount of chromium removal decreased when bed height increased
from 1 m to 2 m. The maximum chromium removal obtained at a bed height of 1 m was 85%.
This bed height was thus selected as the optimal value for chromium removal.

291 **3.4.** Comparison between C/DAFM and BM

In this study a higher percentage of chromium removal was achieved using the C/DAFM than with the BM. The maximum chromium removal obtained with the BM was about 65% when carried out using the optimal conditions of initial pH 3, contact time 120 min, and adsorbent dose of 7g at the initial chromium concentration of 1000 mg/L, whereas with the C/DAFM, maximum chromium removal reached 85% at a pressure of 3 bars, bed height of 1 m, and flotation time 5 min.

298 **4.** Conclusion

The comparative effectiveness of the C/DAFM vs. the BM for removal of Cr(VI) from a solution was studied. With the BM, using dried *S. bevanom* as the biomass, 65% removal was achieved under optimal conditions including initial pH 3, contact time 120 min, and amount of adsorbent 7 g in 500 mL solution. In the C/DAFM system, maximum chromium removal achieved was 85% at optimal conditions including pressure of 3 bars and flotation time of 5 min. Comparison of the two methods demonstrated that for an initial chromium concentration of 1000 mg L⁻¹, the C/DAFM is more effective than the BM.

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347 Figure captions

Fig. 1. Schematic diagram of experimental setup for (a) Schematics of experimental bioreactor designed for removal of MEG from gas-refinery wastewater: (a) air pump, (b) wastewater pump, (c) feed tank, (d) packed bed, and (b) dissolved air flotation method

Fig. 2. (a) Actual measured values vs. those predicted by ANN for Cr(VI) removal, biosorption method; (b) Actual measured values vs. those predicted by ANN for Cr(VI) removal, coagulation-dissolved air flotation method; (c) Effect of initial pH on Cr(VI) removal, constant contact time 150 min, amount of adsorbent 10 g, and Cr (VI) concentration 1000 mg L^{-1}

- **Fig.3.** (a) Effect of contact time on Cr(VI) removal, initial pH 3, amount of adsorbent 10 g,
- and Cr(VI) concentration 1000 mg L⁻¹. (b) Effect of amount of adsorbent on Cr(VI) removal,
- initial pH 3, contact time 120 min, initial Cr(VI) concentration 1000 mg L^{-1}
- **Fig. 4. (a)** Breakthrough curves for Cr(VI) sorption onto *S. bevanom* at different bed heights.
- 361 (b) Effect of flotation time on the C/DAFM at constant pressure of 3 bars and height 20 cm

362

364 **Tables and figures**

365

366 Table 1: Effect of number of neurons in hidden layer on performance of neural network for Cr(VI)

367 removal by biosorption method

Number of neurons in hidden layer	RMSE	R ²
2	1.362	0.996
3	2.183	0.989
4	2.013	0.991
5	1.548	0.994
6	1.536	0.995
7	2.322	0.988
8	6.445	0.902
9	0.884	0.998
10	1.002	0.997

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384	Table 2: Effect of number of neurons in hidden layer on performance of neural network for Cr(VI) by
385	C/DAFM

Number of neurons in hidden layer	RMSE	R^2
2	1.029	0.959
3	1.453	0.909
4	4.678	0.631
5	2.79	0.838
6	9.600	0.605
7	2.090	0.750
8	1.933	0.771
9	0.823	0.971
10	9.23	0.654

Algorithm No.	Algorithm	Transfer Function		RMSE (BM)	RMSE (C/DAFM)	R ² (BM)	R ² (C/DAFM)
		Hidden Layer	Output Layer				
1	BFG	Tansig	Purelin	7.641	2.038	0.859	0.786
2	CGB	Tansig	Purelin	2.376	0.842	0.985	0.970
3	CGF	Tansig	Purelin	1.724	2.262	0.993	0.725
4	CGP	Tansig	Purelin	1.287	2.423	0.996	0.700
5	GDA	Tansig	Purelin	4.549	2.599	0.947	0.688
6	LM	Tansig	Purelin	0.884	0.823	0.998	0.971
7	OSS	Tansig	Purelin	2.072	2.412	0.991	0.759
8	RP	Tansig	Purelin	2.427	2.093	0.986	0.720
9	SCG	Tansig	Purelin	1.461	2.058	0.995	0.771

404Table 3: Root-mean-square errors for training algorithms for 9 neurons in hidden layer of ANN for405Cr(VI) removal by BM and C/DAFM

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Figure 1b

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percentage of Cr (VI) removal (Experimental)

Figure 2b



Figure 2c



Figure 3a



Figure 3b



Figure 4a



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254x190mm (96 x 96 DPI)