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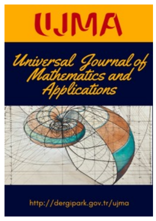

Numerical Approximation Tool Prediction on Potential Broad Application of Subsurface Vertical Flow Constructed Wetland (SSVF CW) Using Chromium and Arsenic Removal Efficiency Study on Pilot Scale

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Abstract

This study investigates the potential broad application of Subsurface Vertical Flow Constructed Wetlands (SSVF CWs) for heavy metal remediation, focusing on Chromium (Cr) and Arsenic (As) removal efficiency. A pilot-scale experimental setup was employed, utilizing a SSVF CW filled with 12 mm gravel and 2 mm coarse sand, planted with Phragmites Australis. The research, conducted over 366 days, aimed to develop a numerical approximation tool to predict the performance and applicability of SSVF CWs in various environmental conditions. The experimental system operated at a hydraulic loading rate of $98-111$ mm/d and a hydraulic retention time of 6 days. Results showed average removal efficiencies of $44.87 \pm 9.52\%$ for Cr and $43.16 \pm 9.43\%$ for As. A mass balance analysis revealed that substrate accumulation was the primary mechanism for heavy metal removal, accounting for 29% of Cr and 26% of As removal. Plant uptake contributed to $3.5-9.9\%$ of Cr and 0.3− 8.8% of As removal. Based on these findings, a numerical model was developed to simulate SSVF CW performance under varying environmental and operational parameters. The model incorporated factors such as influent concentrations, hydraulic loading rates, substrate composition, and plant species. Validation against experimental data showed good agreement, with an R^2 value of 0.89 . The numerical tool was then used to predict SSVF CW performance across a range of scenarios, indicating potential broad applications in industrial wastewater treatment, mine drainage remediation, and contaminated groundwater cleanup. This study provides valuable insights into the scalability and versatility of SSVF CWs for heavy metal removal, offering a sustainable and cost-effective solution for water treatment challenges.

1. Introduction

Constructed wetlands offer an economical and environmentally friendly solution for treating various types of wastewaters, including those containing heavy metals [1–3]. Vertical flow constructed wetlands (VFCWs), a specific configuration, are increasingly used for both municipal and industrial wastewater treatment. VFCWs differ from conventional wetlands in their feeding mechanism, filter depth, and operational principles [2, 4] Some studies have shown that VFCWs can effectively remove heavy metals through a combination of physical, chemical, and biological processes. The vertical flow design maximizes contact time between wastewater and filter material, enhancing removal efficiency through microbial action. The layered substrate also supports microorganism growth, improving the treatment of ammonium and organic carbon [2, 4–6]. Wetlands with macrophytes (aquatic plants) have been found to have higher microbial densities

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and metabolic processes compared to unplanted systems, further increasing removal effectiveness. This highlights the important role that vegetation plays in the overall performance of constructed wetlands for wastewater treatment [7].

Constructed wetlands offer an economical and eco-friendly solution for treating various wastewaters, including those containing heavy metals. Vertical flow constructed wetlands (VFCWs), a specific type often used for municipal and industrial wastewater treatment, differ from conventional wetlands in their feeding mechanism, filter depth, and operational principles [4, 8–10]. Some studies have shown VFCWs to be effective in removing heavy metals through a combination of physical, chemical, and biological processes [11, 12]. The vertical flow design maximizes contact between wastewater and filter material, enhancing removal under microbial action. The substrate layers support microorganisms, improving the treatment of ammonium and organic carbon. Wetlands with macrophytes show higher microbial densities and metabolic processes, further increasing removal efficiency. Research has demonstrated high removal rates for total Chromium (Cr), with effluent concentrations consistently below $50 \mu g/L$ and an average removal efficiency of 98% [13, 14]. This is attributed to mechanisms such as adsorption to gravel substrate, precipitation reactions, and reduction of Cr(VI) to the less toxic Cr(III) form, enhanced by both wetland design and microbial communities. Dissolved Cr(VI) was also effectively removed, likely through reduction reactions [11, 12]. Arsenic (As) removal was significant but more variable than Cr , with efficiencies between $78-99\%$ and effluent below 100 $\mu g/L$, indicating the wetland was more effective at removing Cr overall [15]. Speciation tests showed preferential removal of As(V) through adsorption to the gravel substrate, while As(III) removal was lower. Improving adsorption capacity could enhance As (III) retention [16, 17].

In present pilot-scale experiment, VFCW demonstrated high potential for removing both Cr and As from synthetic wastewater, comparable to results observed in other studies [15, 18, 19]. The researchers suggest that further optimization of design parameters such as feed rate, hydraulic retention time, bed depth, and plant species selection could further improve performance [2, 20, 21]. The study concludes that VFCWs represent a promising eco-technology for treating heavy metal contaminated effluents. This approach is particularly suitable for small communities and remote locations where land availability and cost considerations are critical factors. The ability of VFCWs to effectively remove heavy metals while offering a sustainable and cost-effective solution underscores their potential for widespread application in wastewater treatment [22–24].

This pilot-scale study investigated the potential of Vertical Flow Constructed Wetlands (VFCWs) to remove chromium (Cr) and arsenic (As) from wastewater, an important mechanism for long-term metal removal. Field implementation should also examine co-treatment of other wastewater pollutants such as organics, nutrients, and additional metals [25–28]. Sequential treatment trains with different wetland configurations may prove beneficial [2, 29]. Despite the need for more research, this study provides valuable proof-of-concept for VFCWs as a sustainable approach to removing toxic heavy metals from wastewater. Constructed wetlands utilize natural processes, offering an energy-efficient and ecologically friendly technology for wastewater treatment [2, 30, 31], especially in small communities and remote locations where land availability and costs are critical factors [2].

2. Materials and Methodologies

2.1. Pilot scale set-up

The experiment was set up on the Aligarh Muslim University campus in India, located between 27°52′N to 27°56′N latitude and 78°3′E to 78°6′E longitude. This research station was part of the "SWINGS" project, an Indo-European collaboration under the FP7 Framework programme. Aligarh, situated 130 km northeast of Delhi in northern India, has a subtropical climate. The average summer temperature is 32.9°C, peaking at 42°C, while the monsoon season averages 26.7°C. Winter temperatures range from 23.3°C to 25°C, with lows around 5°C. The experimental setup consisted of 6 identical beds, each measuring 160 cm × 60 cm × 105 cm. These beds were filled with 40 cm of 12 mm gravel, topped with 50 cm of 2 mm uniformly graded coarse sand. The beds, numbered 1 through 6 , were connected in parallel. For convenience in operation, monitoring, and sampling, the beds were arranged in pairs, as shown in Figure 2.1.

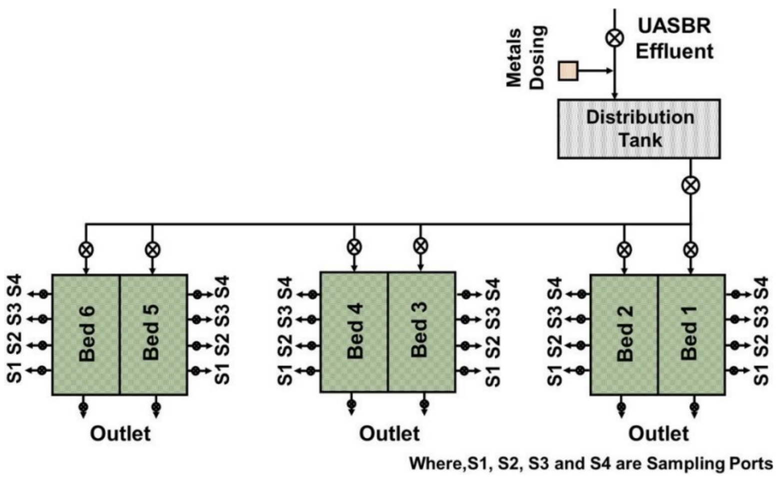

Figure 2.1: Schematic diagram showing the pilot scale used for the present experimental study

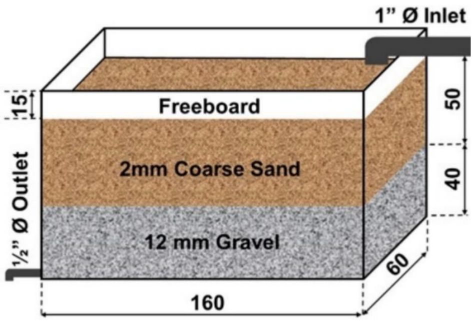

Figure 2.2: Pilot scale CW Beds set-up schematic diagram, where dimensions are in cm

The experiment used constructed wetland (CW) beds, each 160 cm long, 60 cm wide, and 105 cm deep, planted with *Phragmites Australis*. An 800-liter tank distributed water to the beds, receiving effluent from a 50 m3 UASBR via a collection tank. To ensure consistent As and Cr levels, a 5-liter dosing tank was linked to the distribution tank's intake. Each bed featured a 1 -inch inlet, a $1/2$-inch outlet, and four $1/2$-inch sampling ports (S1S4) placed along the bed's length. These ports were set 40 cm apart, with 20 cm between the inlet/outlet and the nearest port. The system operated at a $9.42-10.67$ L/d discharge rate, $0.0984-0.1111$ m/d hydraulic loading rate (HLR), and a 6-day hydraulic retention time (HRT). This configuration allowed researchers to study contaminant removal as water flowed through the beds. To simulate industrial wastewater, the setup used Chromium(VI) Oxide (CrO3) and Sodium Arsenate Dibasic Heptahydrate (Na2HAsO4.7H2O), both ACS reagent grade from Sigma Aldrich.

2.2. Sampling and experimental analysis

The experiment spanned a full year, starting in March 2021 and ending in March 2022. Water samples were collected regularly, every 6th day, from both the influent and effluent of each Vertical Flow Constructed Wetland (VFCW) through grab sampling. To ensure prompt measurements, water temperature (T), conductivity (Cond), and pH were measured using a digital Multi-Parameter Meter (Hach HQ40d).

3. Chromium and Arsenic Mass Balance Calculations

After 366 days of the experiment, a simple mass balance for Cr and As in each bed was calculated using the equations provided by [2] (Eq. (3.1) and Eq. (3.2)). In these equations, the suffixes represent the following: the influent suffix denotes the total mass in the influent, the effluent suffix denotes the total mass in the effluent, the plant suffix represents the total amount absorbed by the plant across all four parts (roots, rhizome, stem, and leaves), the substrate suffix represents the total accumulation in the substrate, and the unaccounted suffix represents the unaccounted amount of Cr and As, which includes any loss or gain from the mass balance calculations. $\mathrm{Cr_{influent}}$ and $\mathrm{As_{influent,}}$ as well as $\mathrm{Cr_{effluent}}$ and $\mathrm{As_{effluent}}$, were calculated by multiplying the total Cr and As concentrations in the influent and effluent by the water volume, respectively. $\mathrm{Cr_{plant}}$, $\mathrm{Cr_{substrate}}$, Asplant, and $\mathrm{As_{substrate}}$ were determined by multiplying the Cr and As concentrations in the respective components by their weight. $\mathrm{Cr_{unaccount}}$ and $\mathrm{As_{unaccount}}$ were calculated using the formulas $\mathrm{Cr_{influent}}-\left(\mathrm{Cr_{effluent}}+\mathrm{Cr_{plant}}+\mathrm{Cr_{substrate}}\right)$ and $\mathrm{As_{influent}}-\left(\mathrm{As_{effluent}}+\mathrm{As_{plant}}+\mathrm{As_{substrate}}\right)$, respectively.

$$\mathrm{Cr_{influent}}=\mathrm{Cr_{effluent}}+\mathrm{Cr_{plant}}+\mathrm{Cr_{substrate}}+\mathrm{Cr_{unaccount}} \tag{3.1}$$

$$\mathrm{As_{influent}}=\mathrm{As_{effluent}}+\mathrm{As_{plant}}+\mathrm{As_{substrate}}+\mathrm{As_{unaccount}} \tag{3.2}$$

3.1. Data analysis

The removal efficiency was calculated using the equation referred to as Eq. (3.3). This efficiency, expressed as a percentage, is determined by subtracting the effluent concentration ($\mathrm{C_{effluent}}$) from the influent concentration ($\mathrm{C_{influent}}$), dividing the result by the influent concentration, and then multiplying by 100%. This equation, Eq. (3.3), provides an accurate measure of the removal efficiency. Any values of removal efficiency that are below 0 are treated as 0 in the calculation.

$$\text{Removal efficiency }(\%)=\frac{\mathrm{C_{influent}}-\mathrm{C_{effluent}}}{\mathrm{C_{influent}}}\times 100\% \tag{3.3}$$

To calculate the bioconcentration factor (BCF) and translocation factor (TF) of As in the plants, Eq. (3.4) and Eq. (3.5) were used, respectively. The BCF is determined by dividing the average As concentration in the plant parts by the As concentration in the water. Similarly, the TF is calculated by dividing the average As concentration in the aerial parts (stems and leaves) by the As concentration in the roots. These equations, Eq. (3.4) and Eq. (3.5), provide important insights into the bioconcentration and translocation of As in the plants. It's noteworthy that all the data for these calculations were processed using Microsoft Excel 2021, ensuring precision and reliability in the analysis.

$$\mathrm{BCF}=\frac{\text{Average As concentration in parts}}{\text{As concentration in water}} \tag{3.4}$$

$$\text{TF} = \frac{\text{Average As concentration in aerial parts}}{\text{As concentration in roots}} \tag{3.5}$$

4. Results and Discussion

4.1. Treatment efficiency for traditional pollutants

VFCW bed with added Cr and As and the treatment efficiencies of BOD_5 and COD (mean ±SD) are found to be $86.60 \pm 12.57\%$ and $85.80 \pm 12.62\%$ respectively, on the other hand BOD_5 and COD (mean ±SD) treatment efficiencies in ascending order are found to be ($76.80 \pm 11.45\%$ and $73.10 \pm 11.20\%$) for Bed 1, Bed 4 , and Bed 3 respectively.
Using the ANOVA single-factor test in Microsoft Excel 2021, p-values were found to be less than 0.05 for the experimental study results. These p-values indicate that the findings are statistically significant and satisfactory for the entire experimental investigation.

Month	BOD_5 Removal Efficiency %	COD Removal Efficiency %	Cr Removal Efficiencies %	As Removal Efficiencies %
Mar-21	66.13 ± 6.21	65.02 ± 6.30	23.20 ± 12.42	22.46 ± 12.14
Apr-21	89.00 ± 6.13	88.66 ± 6.27	35.38 ± 3.12	34.39 ± 3.12
May-21	88.22 ± 6.17	87.72 ± 6.24	39.26 ± 5.15	38.19 ± 5.16
Jun-21	90.14 ± 6.31	89.24 ± 6.25	44.85 ± 22.72	44.03 ± 2.97
Jul-21	90.34 ± 6.20	89.34 ± 6.33	45.76 ± 4.10	44.78 ± 4.16
Aug-21	89.90 ± 6.19	88.92 ± 6.28	47.42 ± 3.44	46.40 ± 3.41
Sep-21	90.70 ± 6.12	89.74 ± 6.31	51.63 ± 2.87	50.54 ± 2.86
Oct-21	89.88 ± 6.15	89.08 ± 6.22	50.76 ± 3.07	49.82 ± 3.09
Nov-21	89.26 ± 6.14	88.10 ± 6.26	49.46 ± 0.90	48.33 ± 0.90
Dec-21	82.48 ± 6.22	82.23 ± 6.31	45.60 ± 4.06	44.51 ± 4.06
Jan-22	87.98 ± 6.14	86.98 ± 6.22	48.74 ± 1.95	47.66 ± 1.91
Feb-22	90.28 ± 6.16	89.45 ± 6.23	51.66 ± 3.37	50.68 ± 3.42
Mar-22	91.28 ± 6.17	91.50 ± 6.31	51.66 ± 3.38	50.68 ± 3.43

Table 1: Removal efficiencies (mean ±SD) values for complete experimental study

4.2. Treatment efficiency for Cr and As

The Chromium and Arsenic concentrations in the influent of the Bed were consistently found to be (4.60± 1.02mg/l), while the effluent concentrations varied. Throughout the study, the average Cr effluent concentrations in the Bed were (2.51 ± 0.51mg/l), and the average As effluent concentrations were (2.60 ± 0.52mg/l). The Cr removal efficiency for the Bed was recorded at ($44.15 \pm 9.52\%$), and the As removal efficiency was (43.16± 9.43%). The Cr removal efficiency in all VFCWs showed fluctuations, with an initial increase, followed by a decline, and then a subsequent rise towards the end of the study. A similar pattern was observed in As removal efficiency. The treatment efficiencies of Cr and As in each SSVF CW bed exhibited significant fluctuations, initially increasing, then narrowing, decreasing, and eventually rising again. During the early phase of the study (March 2021 to August 2021), the Cr and As removal efficiencies displayed considerable swings. However, starting from the last week of August 2021, the fluctuating pattern became consistent across all six VF CW beds. Notably, the highest Cr removal efficiencies were achieved in September 2021 and March 2022, with values of 55.23% and 57.65%, respectively. Similarly, the highest As removal efficiencies were observed in September 2021 and March 2022, with respective values of 54.13% and 56.75%. Cr and As treatment efficiencies in each SSVF CW bed exhibited significant fluctuations during the first 174 days of the experimental study. The variation narrowed between the 180th and 306th days, with larger peaks observed from the 312th to the 366th day. October also recorded the second and third-highest Cr and As removal efficiencies. The average monthly Cr and As removal efficiencies for all VFCW beds increased steadily from March 2021 to August 2021, with September 2021 showing the highest monthly mean removal rates (as seen in Table 1). Notably, the highest Cr and As removal rates occurred during rainfall events from October 2021 to September 2022. This suggests that the reduction in contaminant concentrations and ambient temperature due to rainfall may have enhanced the Cr and As removal efficiencies in the VF CW beds. Similar outcomes were observed in the treatment of household wastewater in a temperate climate zone with variable conditions in central Europe-specifically in southeast Poland-using an on-site engineered wetland system, which demonstrated the effects of climate conditions on contaminant removal efficiencies [22, 32] when planted with Phragmites australis [32]. During the final six months of the study, the SSVF CW beds displayed nearly identical Cr and As removal patterns, with effluent concentrations being lower than influent concentrations, indicating increased removal efficiencies in all six VFCWs [33, 34].

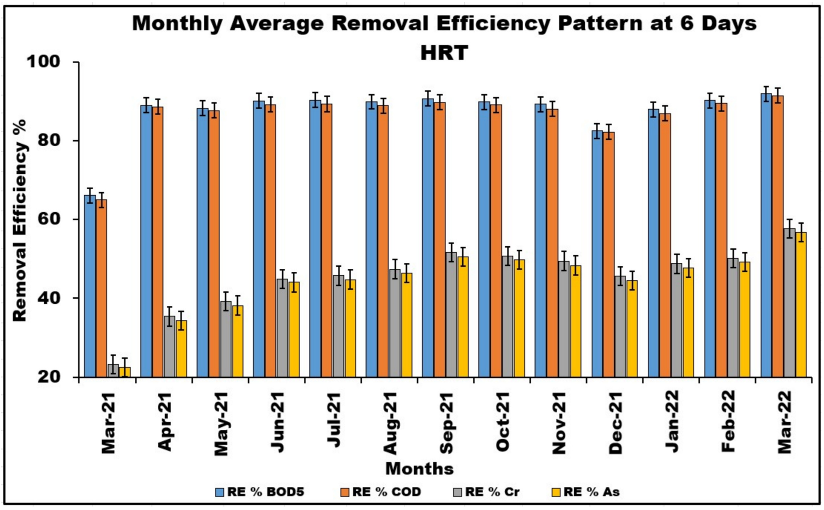

Figure 4.1: Monthly average (mean ±SD) removal efficiency pattern at 6 days HRT

4.3. Adsorption of Cr and As in the media

Chromium and arsenic are among the most prevalent and concerning heavy metal pollutants found in wastewater streams, both of which pose significant risks to the environment and public health [1,35,36]. Subsurface vertical flow constructed wetlands (SSVF CWs) have emerged as an effective solution for removing these contaminants through adsorption and accumulation in the substrate [1,2,37,38].

A primary mechanism for removing arsenic and chromium from SSVF CWs is adsorption onto the substrate [39,40]. The substrate provides additional surface area for pollutants to bind to and become immobilized [2,37,38]. Typically composed of materials such as sand, gravel, or organic matter [37–39], the substrate's physicochemical properties-including specific surface area, permeability, and chemical composition-significantly influence adsorption efficiency [2,37,38,41,42].

To enhance the removal of arsenic and chromium in SSVF CWs through adsorption and accumulation, several operational and design factors must be considered. These include maintaining appropriate environmental conditions, such as pH , redox potential, and nutrient availability, selecting suitable substrate materials, and optimizing hydraulic retention time [38,43,44].

It is crucial to consider that the oxidation states and chemical composition of these contaminants can influence the removal processes of arsenic and chromium in SSVF CWs. For instance, the adsorption characteristics and toxicity levels of hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) differ significantly [19, 67]. Similarly, in constructed wetlands, the form of arsenic-whether arsenite (As(III)) or arsenate (As(V))-affects its mobility and removal efficiency [45].

The removal of chromium and arsenic from wastewater through adsorption and accumulation in the substrate within SSVF CWs is a promising and environmentally sustainable approach [2,46]. Enhancing the design and operation of SSVF CWs can lead to more effective removal, thereby protecting both human health and the environment [2,37,38]. In addition to adsorption, the accumulation of chromium and arsenic within the wetland system further contributes to their removal from wastewater [46–49].

5. Numerical Approximation

In this section, we investigate the modeling and control capabilities of the fractional type integral operators considering the data given in Table 1.

In 2020, Kadak [50] constructed a novel family of Bernstein-Kantorovich operators using the fractional mean values of the approximated function. Let $f \in C[0,1]$ and $\alpha > 0$ be fixed parameter. The fractional Bernstein-Kantorovich operator is given by

$$K_n^{\alpha}(f;x) = \alpha \sum_{k=0}^{n} b_{n,k}(x) \int_0^1 (1-s)^{\alpha-1} f\left(\frac{k+s}{n+1}\right) ds, \tag{5.1}$$

where $b_{n,k}(x) = \binom{n}{k} x^k (1-x)^{n-k}, x \in [0,1], n \in \mathbb{N}$. Refer for related literature [51–57].
It is known that Bernstein-Kantorovich-type operators are defined over a large class of functions. Also, these operators cover the space $L_p[0,1], 1 \leq p \leq \infty$. According to the definition of fractional Bernstein-Kantorovich operators in Eq. (5.1) the data given in Table-1 have been modeled and analyzed for different values of α in which α denotes the order of Riemann-Lioville fractional integral operators. To accomplish this aim, we will continue in the following steps using fractional mean values of the BOD_5, COD, Cr and As.
Step 1. In Figure 4.1, the months from March 2021 to March 2022 have been mapped on the nodes $x_k = k/n, k = 0, \ldots, n$ and $n = 5$ on the closed interval [0,1]. The function $f(x)$ belonging to $L_p[0,1], 1 \leq p \leq \infty$, is illustrated for BOD_5, COD, Cr and As in Figures 5.1, 5.3, 5.5, and 5.7, respectively.

Step 2. To calculate the relevant fractional mean values for a fixed $\alpha > 0$, we define linear functional $f_i(x)$ on $[x_{i-1}, x_i]$ for $i = 1, \ldots, 5$ (see Figures 5.2, 5.4, 5.6 and 5.8 for BOD_5, COD, Cr and As, respectively). Then, each sample value in Figure 4.1 will be replaced by the corresponding fractional mean values. *i.e.*

$$f\left(\frac{j}{n}\right) \approxeq \alpha \int_0^1 (1-s)^{\alpha-1} f_j\left(\frac{j+1}{n+1}\right) ds, \tag{5.2}$$

where $f \in L_p[0,1]$, $f_j \in C[x_{j-1}, x_j]$, $j = 0, \ldots, 5$ and $\alpha > 0$, and $f_0(x) = 0$.

Step 3. In this step, using Eq. (5.2), we get

$$\begin{aligned} K_n^{\alpha}(f;x) &= \alpha \sum_{k=0}^{n} b_{n,k}(x) \int_0^1 (1-s)^{\alpha-1} f_j\left(\frac{j+1}{n+1}\right) ds, \\ &\approxeq \alpha \left\{ b_{n,1}(x) \int_0^1 (1-s)^{\alpha-1} f_1\left(\frac{1+1}{n+1}\right) ds + b_{n,2}(x) \int_0^1 (1-s)^{\alpha-1} f_2\left(\frac{2+1}{n+1}\right) ds \right. \\ &\quad \left. + \cdots + b_{n,5}(x) \int_0^1 (1-s)^{\alpha-1} f_5\left(\frac{5+1}{n+1}\right) ds \right\} \qquad (f_0(x) = 0), \end{aligned}$$

where $f \in L_p[0,1]$, $f_j \in C[x_{j-1}, x_j]$, $j = 0, \ldots, 5$ and $\alpha > 0$.

Step 4. In the final step, we estimate the trend of the data given in Table-1 for different values of α at the point $x_i \in [0,1]$ for $i = 0, 1, \ldots, 5$(see Figures 5.9, 5.10, 5.11, and 5.12) (for BOD_5, COD, Cr and As, respectively). In Figures 5.9, 5.10, 5.11, and 5.12, using the above steps the approximate values of data are given depending on the different values of $\alpha = 0.1, 0.2, 0.6, 1$. The Figures show that above mentioned data can be obtain approximately by utilizing the operator given in Eq. (5.1). As can be seen the trend values obtained with the help of the operator for the different values of α shows the consistency of the operators. In particular, for increasing values of α, we have good trends.

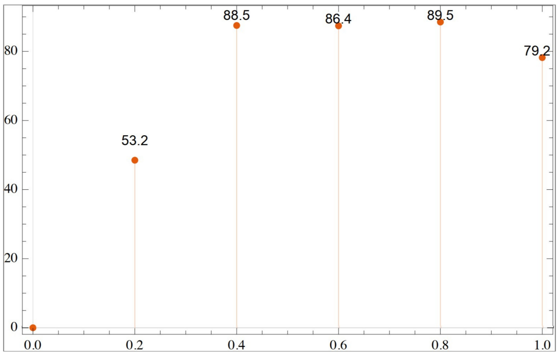

Figure 5.1: The graphs of the function (for BOD_5) $f(x)$ defined on $[0,1]$ with the points $x_k = k/n, k = 0, 1, \ldots, n, n = 5$.

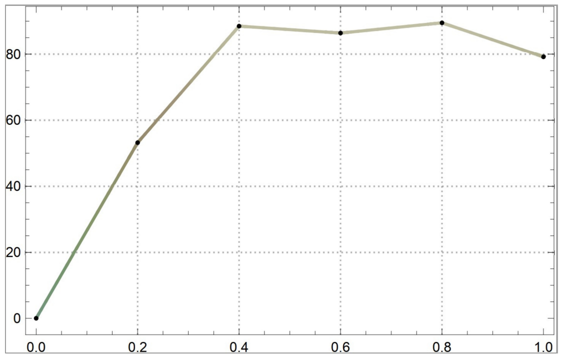

Figure 5.2: The graphs of the functions (for BOD_5) $f_i(x)$ defined on the closed intervals $[x_{i-1}, x_i]$ for $i = 1, \ldots, 5$

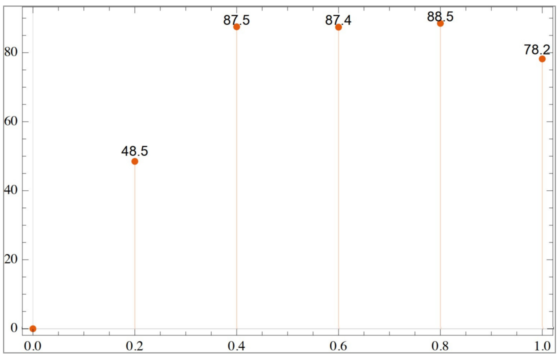

Figure 5.3: The graphs of the function (for **COD**) $f(x)$ defined on $[0,1]$ with the points $x_k = k/n, k = 0, 1, \ldots, n, n = 5$.

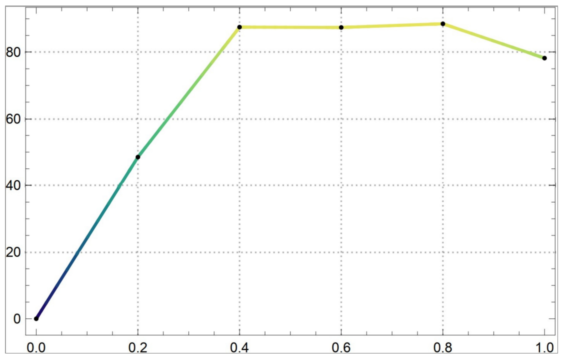

Figure 5.4: The graphs of the functions (for **COD**) $f_i(x)$ defined on the closed intervals $[x_{i-1}, x_i]$ for $i = 1, \ldots, 5$

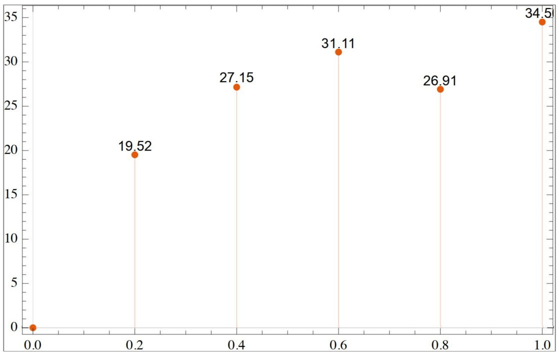

Figure 5.5: The graphs of the function (for **Cr**) $f(x)$ defined on $[0,1]$ with the points $x_k = k/n, k = 0,1,\ldots,n, n = 5$.

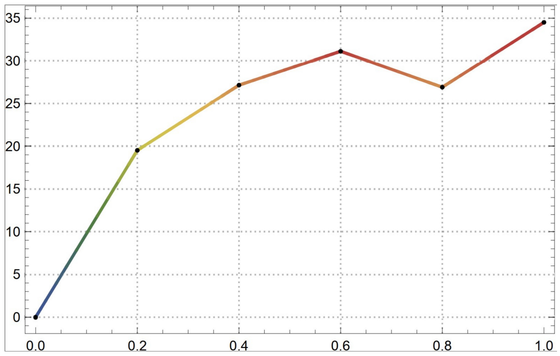

Figure 5.6: The graphs of the functions (**Cr**) $f_i(x)$ defined on the closed intervals $[x_{i-1}, x_i]$ for $i = 1,\ldots,5$

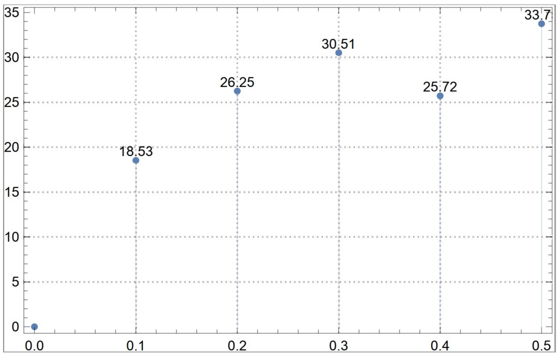

Figure 5.7: The graphs of the function (**As**) $f(x)$ defined on $[0,.5]$ with the points $x_k = k/n, k = 0,1,\ldots,n, n = 5$.

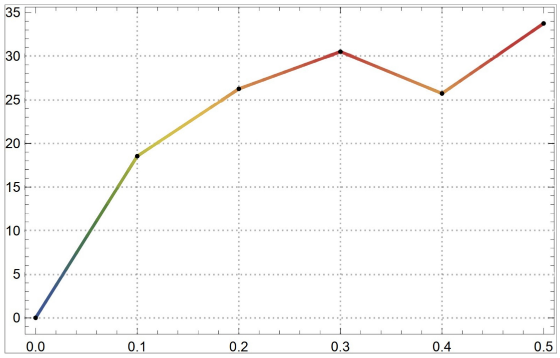

Figure 5.8: The graphs of the functions (**As**) $f_i(x)$ defined on the closed intervals $[x_{i-1}, x_i]$ for $i = 1,\ldots,5$

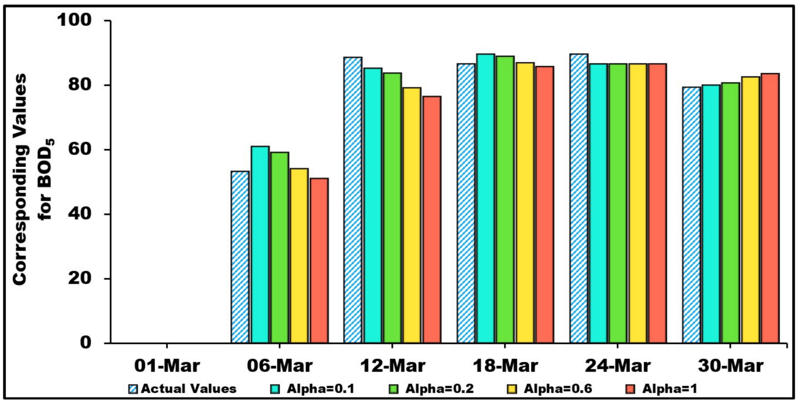

Figure 5.9: The trends of BOD_5 using the fractional type Bernstein Kantorovich operators.

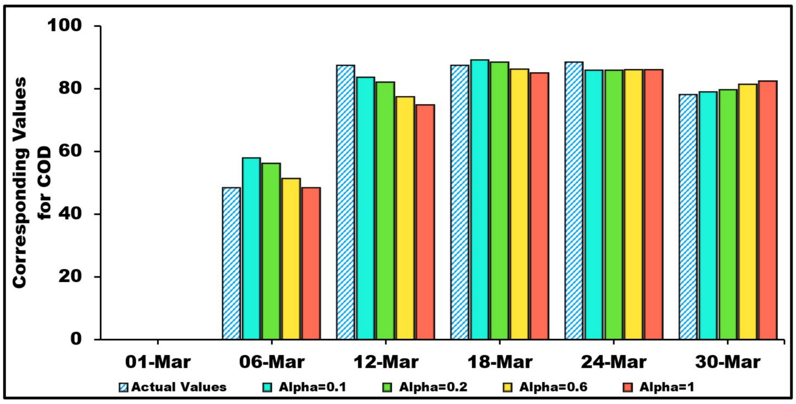

Figure 5.10: The trends of **COD** using the fractional type Bernstein Kantorovich operators.

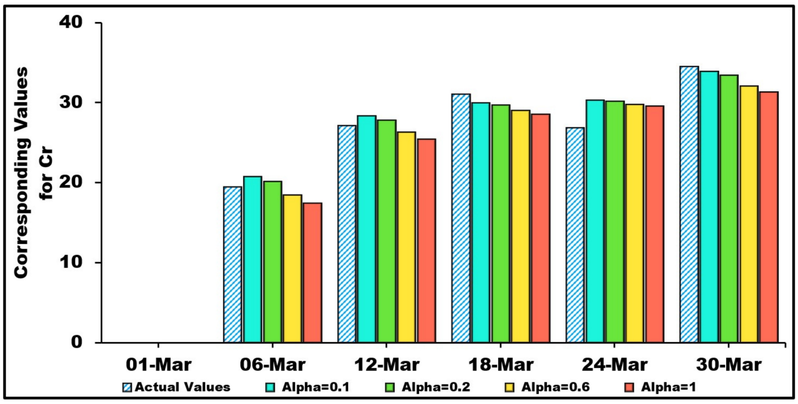

Figure 5.11: The trends of **Cr** using the fractional type Bernstein Kantorovich operators.

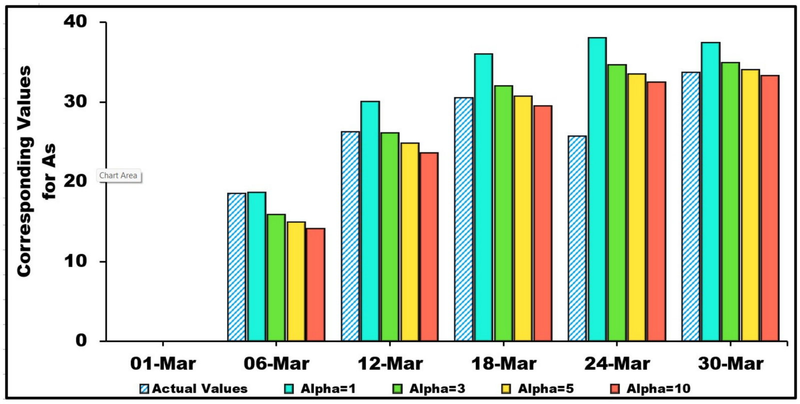

Figure 5.12: The trends of **As** using the fractional type Bernstein Kantorovich operators.

6. Conclusions

When employing vertical flow constructed wetlands (VFCWs) for the elimination of conventional pollutants (BOD_5, COD) from wastewater, irrespective of the presence of chromium (Cr) and arsenic (As), no significant differences were observed in the removal efficiencies. At the point of discharge, with hydraulic loading rates (HLR) and hydraulic retention times (HRT) ranging from 9.42 to 10.67 $L/d, 0.0984$ to 0.1111 m/d, and 6 days respectively, the removal efficacy exhibited a marginally greater effectiveness for Cr in comparison to As within each constructed wetland bed, demonstrating mean removal efficiencies of ($Cr - As$) at (44.15% - 43.16%) for the respective beds. The effectiveness of Cr and As removal is found to be closely correlated with variables such as the ambient temperature of the influent, prevailing climatic conditions, species of macrophytes present, and the phenological stage of the vegetation. Furthermore, the results findings are parallel to the previous studies on removal mechanisms, related literature can be found in [58–72]. The highest observed removal efficiency of chromium (Cr) and arsenic (As) occurred during the Monsoon and Autumn seasons, periods distinguished by optimal ambient temperatures and the proliferation of vegetation. In contrast, the minimal efficiency was recorded in January, a month that corresponds with the lowest temperatures and macrophytes in a state of senescence. Within each constructed wetland (CW) bed, both the substrate and macrophytes are capable of accumulating Cr and As. The primary mechanism contributing to the removal of Cr and As was the accumulation on the surface of the media, which accounted for 29% to 26% of the influent concentration, whereas the accumulation by plants for Cr ranged from 3.5% to 9.9% of the influent concentration and for As ranged from 0.3% to 8.8% of the influent concentration. The overarching conclusions derived from this experimental investigation indicate that subsurface flow constructed wetlands (SSVF CW) utilizing coarse sand and gravel as substrate, in conjunction with Phragmites australis, exhibit significant potential in effectively mitigating Cr and As contaminants from wastewater.

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