Single and binary adsorption experiments and modeling of arsenic and fluoride using activated carbon as adsorbent

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Single and binary adsorption experiments and modeling of arsenic and fluoride using activated carbon as adsorbent

Amrutha Acharya, Gautham Jeppu*, Girish Chikmagalur Raju, Balakrishna Prabhu, Alita Stephy Martis, Shrividya Ramesh

Abstract
Arsenic and fluoride are co-occurring contaminants in groundwater. This research investigated the competitive adsorption of arsenic and fluoride from aqueous solution on activated carbon. Batch experiments were used to study the behavior and efficiency of activated carbon to know the influence of adsorbent dosage, contact time, and solution pH of arsenic and fluoride in single and binary component systems. At optimum values, in single-component systems, activated carbon demonstrates efficient adsorption of arsenic and fluoride, achieving a percentage removal of 93.56% for arsenic and 72% for fluoride. Similarly, in binary-component systems, the percentage removal of As(V) is found to be 71.91%, while fluoride is removed at a rate of 90%. Kinetic studies showed that adsorption followed a pseudo-second-order kinetic mode, which suggests chemisorption. Langmuir, Freundlich, Toth, Redlich Petersons, and Modified Langmuir Freundlich (MLF) models were used to interpret the single adsorption isotherm data. The maximum uptake of arsenic and fluoride was 3.58 mg/g and 2.32 mg/g, respectively. It was noted that the Modified Langmuir Freundlich isotherm model gave a better fit with higher $R^2$ and lower RMSE values. Extended Langmuir and Extended Freundlich isotherm models were used to interpret the competitive adsorption data. The competitive studies showed selectivity of adsorption for As(V) > F which suggested that the affinity of activated carbon was greater towards As(V) than fluoride. Also, As(V) showed antagonistic behavior with F.

Keywords: Competitive Adsorption, Activated Carbon, Arsenic, Fluoride, Binary adsorption, Kinetics, Competitive adsorption isotherms, Equilibrium isotherm modeling

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Novelty

1. Studies focusing on the pH-dependent competitive behavior of arsenic and fluoride are scarce, indicating a research gap in understanding their co-existence.

2. The Modified Langmuir Freundlich isotherm (MLF) model has been utilized to analyze the pH-dependent of fluoride in this study, which has not been done earlier.

3. Limited research has been conducted on the competitive adsorption modeling of arsenic and fluoride using activated carbon as an adsorbent, presenting a novelty for exploration.

4. The Extended Langmuir isotherm model was employed to simulate competitive isotherm parameters.
1. Introduction

In today's world, arsenic and fluoride, as inorganic pollutants in our groundwater, pose a significant threat to the global population. These toxic elements have gained notoriety due to their widespread occurrence and detrimental effects on human health. Heavy metals in water have adversely impacted communities across various nations, leading to severe consequences for the affected individuals. For several decades, countries such as India, Mexico, Argentina, Australia, Pakistan, and Japan have grappled with the co-occurrence of arsenic and fluoride in their groundwater sources. These pollutants seriously challenge public health and necessitate action to mitigate their effects (Y. Yu et al. 2019). When individuals consume water contaminated with arsenic, they face various health risks. This includes an increased likelihood of developing cancer, liver disease, diabetes, and damage to the nervous system. Additionally, individuals may experience complications such as hearing problems, loss of limb sensation, and digestive difficulties (Xu et al. 2002).

Excessive fluoride concentrations in drinking water have also proven detrimental to human well-being. The health problems associated with high fluoride levels include tooth decay and dental fluorosis. Furthermore, fluoride can cause skeletal fluorosis, which damages bones and joints. It has also been linked to thyroid problems, neurological issues, high blood pressure, myocardial damage, cardiac insufficiency, arteriosclerosis, arterial calcification, and heart failure (Bibi et al. 2017). The World Health Organization (WHO) has established limits for arsenic and fluoride in drinking water to address these pressing concerns. The recommended limit for arsenic is 0.01 mg/L, while for fluoride, it is 1.5 mg/L (Prabhu et al. 2021). These guidelines serve as crucial benchmarks for governments and regulatory bodies in implementing measures to ensure safe drinking water for their populations.

The prevalence of excess arsenic in wastewater and drinking water is a significant concern in numerous regions. Extensive research, as highlighted in the literature, has identified several successful adsorbents capable of removing arsenic, such as activated carbon, novel iron, and iron-zirconium-modified activated carbon derived from Tectona grandis sawdust (Sahu et al. 2021). These materials have demonstrated exceptional arsenic removal capabilities. While anthropogenic activities and industrial discharge contribute to the presence of arsenic in water systems, it is crucial to recognize that natural sources also play a role. Weathering, erosion of rocks and soils, and volcanic emissions are among the biological processes contributing to arsenic contamination in aqueous systems (Basu et al. 2015). Arsenic exists naturally in various mineral forms and as an elemental component, with over 200 minerals identified. One of the sources of arsenic contamination in drinking water is its geological presence in local bedrock (Lata & Samadder 2016). Addressing the issue of excess arsenic in water systems requires a comprehensive approach encompassing both natural and anthropogenic sources. Additionally, mitigating the impact of natural sources through appropriate water management strategies and geological assessments can help minimize arsenic contamination (Dambies 2005).

The mining industry in several regions has achieved notable development, resulting in the generation of a significant volume of coal mine water during extraction. The area is abundant in fluorine-rich rocks and minerals, which undergo long-term physical and chemical transformations due to prolonged geological processes, causing the fluoride to transition from a stable state to an active state. As mine water percolates through these rocks, it absorbs substantial amounts of fluoride, leading to a high concentration in the coal mine water. Unfortunately, the
improper discharge of mine wastewater has led to the migration of fluoride into surface water bodies, resulting in excessive fluoride levels in these water sources. Hence, considerable efforts have been dedicated to removing fluoride (Y. Xiang et al. 2022). Various composite materials have been employed for this purpose, yielding promising outcomes. For instance, modified Hydroxyapatite, aluminium alginate, activated alumina, zirconium oxide, chitosan composite, and impregnated lanthanum silica gel have demonstrated effective fluoride removal capabilities (W. Xiang et al. 2014). In addition, researchers have explored biopolymers as a cost-effective and economically viable solution for fluoride removal. Notably, a synthesized aerogel composite comprising aluminum-humic acid-lanthanum has exhibited significant efficacy in removing fluoride (Liu et al. 2016). Moreover, literature surveys have revealed that activated carbon derived from diverse materials has been extensively utilized by researchers to eliminate fluoride from aqueous solutions (Karthikeyan & Elango 2008).

The presence of arsenic and fluoride as toxic inorganic pollutants, their co-occurrence in groundwater, and the associated health risks underscore the need for comprehensive strategies to combat this global problem. Given the detrimental effects of arsenic and fluoride contamination, it is crucial to delve into research concerning their simultaneous adsorption. Activated carbon has proven highly effective in various adsorption processes, particularly in removing pollutants from water. This versatile material possesses exceptional adsorption capabilities owing to its large surface area and porous structure (Jing et al. 2012). Moreover, activated carbon offers an economical solution for fluoride removal, making it an attractive option for water treatment (He et al. 2020). Studies have explored the simultaneous removal of arsenic and fluoride using commercially available powders such as hydrated cement, brick, and marble as adsorbents. Among these powders, hydrated cement exhibited the highest removal efficiency, reaching 90% compared to the other two adsorbents (Bibi et al. 2015)—also, investigations involving treated laterite as an adsorbent demonstrated promising results for simultaneous arsenic and fluoride removal. Whereas the binary system did not significantly impact arsenic, fluoride exhibited antagonistic behaviour (Rathore et al. 2016).

Innovative approaches have also been explored, such as impregnating sawdust with ferric hydroxide and activated alumina for maximum sorption of arsenic and fluoride. Column studies at a pH of 6.5 effectively removed both contaminants (Dhanasekaran & Sahu 2021). Additionally, synthesizing different hydrogels and chitosan has provided promising arsenic and fluoride uptake results. The maximum adsorption capacities of 0.0022 mg/g for arsenic and 0.150 mg/g for fluoride were reported (Burillo et al. 2021).

Although the literature on the multi-component adsorption of arsenic and fluoride with model studies is limited, the competitive adsorption of these contaminants is underscored by their occurrence in various locations. The analysis of competitive adsorption is imperative to devise effective strategies for water treatment and ensure the removal of both arsenic and fluoride. The exploration of novel adsorbents, optimization of conditions, and thorough understanding of the competitive adsorption process is necessary to develop efficient and sustainable solutions for combating arsenic and fluoride contamination in water resources. Further research in this area will contribute to enhanced water treatment technologies, safeguarding the well-being of communities affected by these pollutants.
There is minimal information in the literature regarding the competitive adsorption of arsenic and fluoride with modeling approaches. The single-component isotherm models such as Langmuir, Freundlich, modified Langmuir isotherm, Toth, and Redlich-Peterson's model were modeled in this study. The study also utilizes Extended Langmuir and Extended Freundlich isotherm models to simulate adsorption for multi-component systems. These models provide insights into the maximum adsorption capacity, parameters, affinity, and interaction of component systems during adsorption. These models play a crucial role in understanding the adsorption process and the behavior exhibited by arsenic and fluoride in competitive systems. These models can also determine synergetic, antagonistic, and no-interaction behavior. Additionally, the study explores the interaction mechanisms, kinetics, competitive isotherm modeling, and adsorption properties by analyzing the adsorbent's and adsorbate's equilibrium data. By comprehensively examining the adsorption behavior of arsenic and fluoride on activated carbon, this study contributes to a deeper understanding of their removal mechanisms. The findings from this research have the potential to inform the development of efficient adsorption processes and provide valuable insights for water treatment applications.

This study aims to investigate the efficacy of activated carbon in adsorbing the toxic pollutants arsenic and fluoride in single and simultaneous systems. Furthermore, it explores various characterization techniques employed to evaluate the properties of activated carbon. The equilibrium studies and different adsorption isotherm models are implied to elucidate the sorption mechanism.

2. Materials and methods

2.1 Chemical and reagents

Na$_2$HAsO$_4$·7H$_2$O and NaF were used to prepare the standard samples of arsenic and fluoride. NaOH or HCl was used to optimize the pH of the solution. The activated carbon was purchased from Darco, USA. The activated carbon is granular and insoluble. The purchased activated carbon has a selectivity range of up to 57, particle size 12-20 mesh, and high purity grades from Sigma Aldrich.

2.2 Characterization of activated Carbon

The characterization of adsorbents activated carbon was carried out by Brunauer Emmett Teller (BET) apparatus, X-ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), and Energy Dispersive Spectroscopy (EDS). BET apparatus (Smart Instruments, Mumbai) gives the surface area and pore volume. The XRD (EMPyrean range, Malvern PANalytical, Netherlands) is a non-destructive technique recognizing crystal phases and structure. FESEM (FEI. Quanta 200, Thermofisher, USA) investigates morphology and orientation. The compositional and topographic information was studied by EDS (Irtracer 100, Shimadzu, USA).

2.3 Adsorption Kinetics and Isotherms

The single and binary adsorption studies of As(V) and F ions onto activated carbon were conducted in batch mode at 25±2°C. In a typical procedure for single kinetic experiments, 250mL of solute concentration was taken in 250mL conical flasks, and 1.25 g of activated carbon was added at pH value 5±0.02. The flasks were kept in an incubator shaker at 250 rpm. The aliquots are taken at regular intervals of time up to 4 days. Similarly, adsorption isotherm experiments are conducted with different initial concentrations of 1 to 100 mg/L by adding 5 g/L of
activated carbon to 50-100 mL solution in 250 mL conical flasks with pH 5±0.02 at 25±2°C for 48 hours. Then, the solution is filtered by microfilters. A flame atomic absorption spectrophotometer measures the concentration of arsenic, and a Thermo Orion Ion-Selective Fluoride meter determines fluoride concentration. The effect of pH on the adsorption capacity of activated carbon is determined by adjusting the pH range of 3 to 11; initial concentrations were 10 mg/L for As (V) & F. Finally, the metal ion adsorption at equilibrium onto activated carbon in aqueous solution is given by the equation:

\[ Q_e = \frac{(C_0 - C_e)V}{m} \]  

Eq. (1)

Where \( C_0 \) is the initial concentration (mg/L), \( C_e \) is the final concentration (mg/L), \( V \) is the volume of aqueous solution (L), and \( m \) is the adsorbent dosage (g/L).

The binary adsorption systems were prepared with the same operating conditions as single systems. The kinetics and isotherm experiments are conducted in triplicates; the average with standard deviation values are considered. The pseudo-first-order, pseudo-second-order, and Elovich kinetic models are predicted for single and binary systems. Langmuir, Freundlich, Modified Langmuir Freundlich, Toth, and Redlich Peterson isotherm models are modeled for single-component systems. The competitive Extended Langmuir isotherm model is modeled for binary systems.

The pseudo-first-order kinetics model,

\[ q_t = q_e (1 - e^{-k_L t}) \]  

Eq. (2)

Where \( k_L \) (min\(^{-1}\)) is the coefficient of pseudo-first-order adsorption rate, \( q_e \) and \( q_t \) are the ion adsorbed (mg/g) quantity at equilibrium and time \( t \), respectively.
The pseudo-second-order kinetics model,

\[ q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \] Eq. (3)

Where \( K_2 \) is the pseudo-second-order rate constant (g/mg min), \( q_e \) and \( q_t \) are the quantity of ion adsorbed (mg/g) at equilibrium and time \( t \), respectively.

The Elovich equation kinetics model,

\[ q_t = \frac{1}{b} \ln (1 + abt) \] Eq. (4)

Where \( q_t \) is the adsorbate concentration at any time, \( t \), per weight of adsorbent (mg/g), \( a \) is the Elovich constant related to the initial adsorption rate (mg/g.min), \( b \) is the Elovich constant related to the desorption rate (g/mg).

The intraparticle diffusion model,

\[ q_t = k_i t^{0.5} + C \] Eq. (5)

Where \( k_i \) is the intraparticle diffusion rate constant (g mg\(^{-1}\) min\(^{-1/2}\)), and \( C \) is the surface adsorption.

The Langmuir isotherm model is given by,

\[ Q_e = Q_m \frac{k_L C_e}{1 + K_L C_e} \] Eq. (6)

Where \( C_e \) is the adsorbate concentration at equilibrium (mg/L), \( q_e \) is the Equilibrium adsorption capacity of adsorbents (mg/g), \( Q_m \) is the maximum adsorption capacity (mg/g), \( K_L \) is the Langmuir constant expressed as L/mg, and \( C_0 \) is the initial concentration of the solution expressed as mg/L. The adsorbent sites will have the same energy to attract the adsorbates. It assumes the formation of a monolayer, homogenous surface, and no interactions between the adsorbates (Li et al. 2003).

The Freundlich Isotherm model is given by,

\[ Q_e = K_F C_e^{1/n} \] Eq. (7)

\( K_F \) is adsorption capacity (L/mg), and \( 1/n \) is adsorption intensity. It indicates relative energy distribution and the adsorbate sites' heterogeneity. The value of \( 1/n \) indicates the favorability of the adsorption, i.e., if \( 1/n \) is greater than 0, or \( 0 < 1/n < 1 \), then adsorption is favorable, and when \( 1/n = 1 \), adsorption does not occur. A reversible multilayer on the heterogeneous surface is established. The distribution of components depends on the time and energy of the sites ensured (Ofudje et al. 2020).
The Redlich Peterson Isotherm model is given by,

\[ q_e = \frac{k_{RP} C_e}{1 + k_{RP} C_e^\beta} \quad \text{Eq. (8)} \]

\( k_{RP} \) and \( \alpha_{RP} \) are the Redlich-Peterson isotherm model constants, and \( \beta \) is the exponent of the Redlich-Peterson isotherm, which lies between 0 and 1. It obeys Langmuir and Freundlich models, but it is not monolayer adsorption. It pertains to homogeneous or heterogeneous surfaces (Al-Ghouti & Da’ana 2020).

The Toth Isotherm model is given by,

\[ q_e = \frac{K_T C_e}{(\alpha_T + C_e)^\gamma} \quad \text{Eq. (9)} \]

\( K_T \) and \( \alpha_T \) are the Toth isotherm model constants, and \( \gamma \) is the exponent of the Toth isotherm, which lies between 0 and 1. It has the vital function of operating both in low and high concentrations. Langmuir model is modified to diminish the errors between experimental and predicted data (Girish 2019).

The Modified Langmuir Freundlich Isotherm (MLF) model (Jeppu & Clement 2012) is given by,

\[ Q_e = Q_m \left( \frac{[C_e K_a]^n}{1 + [C_e K_a]^n} \right) \quad \text{Eq. (10)} \]

\( Q_m \) is the maximum adsorption capacity of the system (mg/g), \( C_e \) is the aqueous phase concentration at equilibrium (mg/L), \( K_a \) is the affinity constant for adsorption (L/mg), and \( n \) is the index of heterogeneity. In the above equation, the affinity constant \( (K_a) \) value can be varied for pH-dependent sorption effects. The uniqueness of this isotherm is its pH dependency on adsorption systems. The essential experimental condition required to apply this isotherm model in a system is pH (Jeppu & Clement 2012).

An extension of single-component adsorption isotherms is multicomponent adsorption isotherms. Based on the single adsorption isotherm, the multicomponent isotherm is derived. This work uses the multicomponent adsorption isotherms described below to analyze the experimental data.

The Extended Langmuir Isotherm/Non-Modified Langmuir Isotherm model (EL):

\[ Q_{e, i} = Q_{m, i} \frac{K_{L, i} C_{e, i}}{1 + \sum_{j=1}^{N} K_{L, i} C_{e, i}} \quad \text{Eq. (11)} \]

Where \( Q_{e, i} \) and \( Q_{e, j} \) is the equilibrium adsorption capacity for components i and j (mg/g), \( Q_{m, i} \) and \( Q_{m, j} \) is the maximum adsorption capacity for components i and j (mg/g), \( K_{L, i} \) and \( K_{L, j} \) is the Langmuir constant for
components i and j (L/mg) and \(c_{e,i}\) and \(c_{e,j}\) is the equilibrium concentration for components i and j (mg/L), respectively. The active sites on the adsorbent are assumed to be uniform and to have the same energy in this model. Pollutant molecules also adhere to the active sites due to the adsorbates' non-interacting action. The drawback of this approach is that the values of the isotherm parameters for other adsorption systems might be drastically different (Berber-Mendoza et al. 2018).

The Extended Freundlich Isotherm Model (EF):

\[
Q_{e,i} = \frac{K_{F,i}c_{e,i}^{(1/n_i)+x_i}}{c_{e,i}^{x_i} + y_iC_{e,i}^{z_i}} \\
Q_{e,j} = \frac{K_{F,j}c_{e,j}^{(1/n_j)+x_j}}{c_{e,j}^{x_j} + y_jC_{e,j}^{z_j}}
\]

Eq. (14)

Where \(Q_{e,i}\) and \(Q_{e,j}\) is the equilibrium adsorption capacity for components i and j (mg/g), \(n_i\) and \(n_j\) is the adsorption intensity for components i and j (mg/g), \(K_{F,i}\) and \(K_{F,j}\) is the Freundlich constant for component i and j (L/mg), \(x_i\) and \(x_j\) are the experimental constant values of a plot \(Q_{e,i}\) and \(c_{e,i}\), \(y_i\) and \(y_j\) are the experimental constant values of a plot \(Q_{e,j}\) and \(c_{e,j}\), \(z_i\) and \(z_j\) are the experimental constant values of a plot \(Q_{e,i}\) and \(c_{e,i}\), respectively. The primary assumption in this model is that interaction happens among the adsorbed molecules. It uses the single-component Freundlich isotherm parameters, interactions, and competition factors. A disadvantage of this model is that 6 and 4 other fitting parameters are required for a binary system (Padilla-Ortega et al. 2013).

Analytical errors

The least-square fit was used to assess the model parameters, and it becomes essential to compare error distribution. The sum of square errors is minimized while calculating the model parameter. The correlation coefficients and \(R^2\) values are typically used to determine whether a model is acceptable. To this purpose, the root mean square error (RMSE) and the sum of square error (SSE) error functions (Eq 15 and Eq 16) were utilized to validate the fitness of the models examined in the current investigations (Ofudje et al. 2020).

\[
SSE = \sum_{i=1}^{N} (Q_{exp} - Q_{cal})^2
\]

Eq. (15)

\[
RMSE = \sqrt{\frac{\sum_{i=1}^{N} (Q_{exp} - Q_{cal})^2}{N}}
\]

Eq. (16)

\(N\) is the number of experimental data points. The lower the values of SSE and RMSE and the greater the \(R^2\), the more model is suitable.
3. Results and Discussion

3.1 Characterization of adsorbent

The surface area and pore volume of activated carbon was determined using the Brunauer Emmett Teller (BET) apparatus, which plays a significant role in adsorption due to the availability of active sites on adsorbents. In this study, the activated carbon exhibited a BET surface area of 568.14 m$^2$/g and a pore volume of 0.4507 cc/g. The average pore size of the activated carbon was calculated to be 3.1731 nm, indicating that it falls within the mesopore range. Previous works have obtained similar results (Arshadi et al. 2014; Deng et al. 2019; Kakavandi et al. 2016; Oveisi et al. 2018; D. Yu et al. 2018).

The Field Emission Scanning Electron Microscopy (FESEM) technique was employed to determine the morphology and orientation of the adsorbent. Figure 3(a) displays the FESEM images of plain activated carbon magnified at 25kX. The images reveal a uniform and porous surface for the activated carbon, as reported in previous studies (Kumar & Jena 2016; Nodeh et al. 2020).

The Energy Dispersive X-ray Spectroscopy (EDS) technique provides compositional and topographic information about materials. The EDS spectrum in Figure 3(a) confirmed the presence of essential elements such as carbon and oxygen in the activated carbon. The intense spectrum of activated carbon was observed within the 0-1 KeV range, and the peaks in the EDS spectrum indicated the presence of carbon. The atomic percentage of carbon was found to be 33.33%, while oxygen accounted for 66.67% of the activated carbon composition. The same results were obtained in previous studies (Baig et al. 2009; Luo et al. 2019; Merrikhpour & Jalali 2013; Saikia et al. 2017).

The X-ray Diffraction (XRD) pattern of activated carbon exhibited two major diffraction peaks at $2\theta = 21.92^\circ$ and $44.05^\circ$, corresponding to the (002) and (100) planes, respectively. These peaks align well with the JCPDS file 41–1487, indicating that the activated carbon possesses an amorphous and graphitic structure. Previous studies have also reported this observation (Kalagatur et al. 2017; Rodrigues et al. 2020). The average particle size of activated carbon was determined using the Scherrer equation, considering the peak locations, which resulted in an average particle size of 1.102 nm.
3.2 Percentage removal of arsenic and fluoride in single and binary component systems

In the single-component system, adsorption experiments were performed for As(V) and F using activated carbon as the adsorbent. The experiments were conducted with a volume (V) of 50 mL, pH value of 5, dosage ranging from 1 to 10 g/L, temperature (t) set at 25 °C, initial concentration (Co) of 100 mg/L, and agitation speed of 150 rpm. Similarly, in the binary-component system, adsorption experiments were carried out for As(V) and F using the same conditions as mentioned above: a volume (V) of 50 mL, pH value of 5, dosage ranging from 1 to 10 g/L, temperature (t) set at 25 °C, initial concentration (Co) of 100 mg/L, and agitation speed of 150 rpm. The adsorbent used in both cases was activated carbon.

The influence of contact time on the percentage removal of arsenic and fluoride in single and binary component systems by activated carbon is shown in Fig 4 and Fig 5. In a single-component system, the percentage removal of arsenic increased with increasing contact times until 48 h, which remained constant, as shown in Fig 4a. Similarly, the percentage removal of arsenic in the binary component system increased with increasing contact time up to 30 h, and after that, it became constant, as shown in Fig 4b. The percentage removal of fluoride increased with the increasing contact time till 24 h, after which the percentage removal continued until saturation with the increasing contact time shown in Fig 5a. Similarly, the percentage removal of fluoride in the binary
component system increased with the increasing contact time till 30 h. After that, the percentage removal of fluoride becomes constant with the increasing contact time, as in Fig 5b. The experiment initially observed the highest reduction of arsenic and fluoride levels. This can be attributed to the abundance of vacant sites on the adsorbent surface during the early stages of the experiment. As a result, the adsorption rate during this period was more noticeable. Therefore, the optimal contact time for arsenic and fluoride adsorption was estimated as 48 hours in both single-component and binary-component systems. In the single-component system, the study achieved a percentage removal of 93.56% for arsenic and 72% for fluoride. Similarly, in the binary-component system, the percentage removal of As(V) was found to be 71.91%, while fluoride was removed at a rate of 90%.

![Fig. 4. Influence of contact time on percentage removal of arsenic in a) single and b) binary component systems](image)

![Fig. 5. Influence of contact time on percentage removal of fluoride in a) single and b) binary component systems](image)

### 3.3 Influence of adsorbent dosage on the removal of arsenic and fluoride in single and binary component systems

In the single-component system, adsorption experiments were conducted using activated carbon as the adsorbent at specific conditions: volume (V) of 50 mL, pH value of 5, dosage ranging from 1 to 10 g/L, temperature (t) of 25 °C, initial concentration (Co) of 100 mg/L, and agitation speed of 150 rpm. Similarly, adsorption experiments were carried out under the same conditions in the binary-component system. The impact of adsorbent dosage on the removal of arsenic and fluoride in both single-component and binary-
component systems using activated carbon is illustrated in Figure 6 and Figure 7. Figure 6a represents the 
percentage removal efficiency of arsenic in the single-component system, while Figure 6b shows the removal 
efficiency of arsenic in the binary-component system. The percentage removal efficiency of fluoride in the single-
component system is depicted in Figure 7a, and Figure 7b presents the removal efficiency of fluoride in the binary-
component system.

It is observed that the adsorption rate is more significant when a higher dosage of activated carbon is used. The 
removal efficiencies of arsenic and fluoride in single and binary component systems increase as the adsorbent 
dosage increases. This can be attributed to an increase in the number of active sites and distribution coefficients, 
promoting interactions between the adsorbent and adsorbate as the dosage of the adsorbent increases. 
Consequently, the removal efficiency also rises with increased adsorbent dosage. Based on the results obtained 
from the experiments conducted on single and binary systems, the optimal adsorbent dosage for As(V) and F was 
determined to be 5 g/L.

3.4 Influence of pH on the removal of arsenic and fluoride in single and binary component systems

By using 50 ml of a 0.1M NaCl solution, the point of zero charge ($pH_{zpc}$) of AC was ascertained. The pH was 
maintained between 3 and 11 by adding HCl and NaOH. After adding the activated carbon to the mixture, the pH 
of the mix was assessed after 24 hours. The $pH_{zpc}$ value was determined by the plot $\Delta pH$ versus initial pH. The 
difference between the initial and final pH is known as the $pH_{zpc}$. The point of zero charge for activated carbon is 
seen in Fig. 8.
Fig. 8. Determination of point of zero charges using activated carbon as adsorbent (V=50 mL, t=25 °C, pH = 3 to 11, Dosage = 5 g/L, Co = 0.1 M NaCl at 150 rpm for 24hrs).

From Fig. 8, it can be depicted that activated carbon's zeta potential changes. The activated carbon exhibits a point of zero charge (pHzpc) at approximately pH 6.8. Zeta potential may be used to analyze a material's surface charge (Salih et al. 2020). As a result, the surface of activated carbon is positively charged if the pH of the solution is less than pHzpc (6.8). The surface of AC does not show any charge if the pH of the solution is equal to pHzpc (6.8). Additionally, the surface of activated carbon is negatively charged if the solution's pH is higher than pHzpc (6.8). Therefore, pH plays a vital role in the adsorption process.

Fig. 9. Effect of pH on adsorption of a) As(V) and b) F for the single and binary system (V=50 mL, t=25 °C, pH = 3 to 11, Dosage = 5 g/L, Co = 10 mg/L at 150 rpm using activated carbon as adsorbent)
In this work, Fig 9a and b findings show that As(V) and F adsorption rises as pH lowers. The equilibrium adsorption of arsenic in a single and binary component system is given in Fig 9a. The equilibrium adsorption of fluoride in a single and binary component system is shown in Fig 9b. At pH 3, adsorption was at its highest; as pH increased, adsorption was reduced. Similarly, the maximum adsorption was attained at pH 3 according to experimental findings for F adsorption utilizing AC. The As(V) and F were adsorbed at a lower rate when the pH of the solution increased. It may result from the adsorbent’s surface becoming negatively charged when the pH rises. As(V) and F exhibit a similar considerable adsorption reduction with increasing pH in a binary system, as in Fig. 9.

3.5 Adsorption isotherm studies

3.5.1 Kinetic of metal ions for single component adsorption

The results of kinetic adsorption studies with the function of contact time for As (V) and F in a single component system are given in Figs 10 and 11. It shows that As(V) adsorption on activated carbon was more than that of fluoride in a single-component system. Initially, the adsorption was slow, then the adsorption process increased up to 24hrs, reaching equilibrium. The experimental conditions for the kinetics were the initial concentrations $C_o = 10$ ppm, the volume of solution taken is 250 mL, pH=5, the dosage of adsorbents taken is 5 g/L, agitation=200 rpm, and temperature is 25 °C of a fluoride and arsenic solution.

![Fig. 10. Kinetic adsorption model fit of As(V) in single component system (V=250 mL, t=25 °C, pH = 5, Dosage = 5 g/L, Co = 10 mg/L at 200 rpm using activated carbon as adsorbent)](image-url)
Fig. 11. Kinetic adsorption model fit of fluoride in the single component system (V=250 mL, t=25 °C, pH = 5,
Dosage = 5 g/L, Co = 10 mg/L at 200rpm using activated carbon as adsorbent)

Fig. 12. Test of the pseudo-First-order equation for a) As(V) and b) F in the single component system
Fig. 13. Test of the pseudo-second-order equation for a) As(V) and b) F in the single component system

Fig. 14. Test of the Elovich equation for a) As(V) and b) F in the single-component system

Fig. 15. Test of the Intra-particle diffusion equation for a) As(V) and b) F in the single-component system

Table 1. Adsorption parameters of a kinetic model of As(V) and F in the single and binary component system by activated carbon.

<table>
<thead>
<tr>
<th>No</th>
<th>Kinetic Model</th>
<th>Parameters</th>
<th>As(V)</th>
<th>F</th>
</tr>
</thead>
</table>

443
444
445
The parameters of adsorption kinetics are given in Table 1 for a single-component system of As(V) and F. The linear relationship between log (q<sub>e</sub>-q<sub>t</sub>) vs. t for As(V) and F did not fit well, as given in Fig 6, indicating that adsorption involves more than one mechanism. Likewise, the relationship between ln(t) vs. t for As(V) and F was not linear, as in Fig 8.

The coefficient of determination (R<sup>2</sup>) is closer to 1 in a pseudo-second-order reaction (Arup Roy 2013). So, the adsorption process attributes pseudo-second-order reaction. The t/q<sub>t</sub> vs. t values show linearity for the pseudo-second-order equation. The pseudo-second-order equation approximates the kinetics of specific chemical reactions, particularly those involving adsorption processes. It assumes a chemisorption mechanism, where the adsorbate species interacts with the surface through chemical bonds. Additionally, it assumes that the rate of site occupation is proportional to the square of the number of unoccupied sites, which is a characteristic of specific adsorption processes. In the pseudo-second-order equation, the rate constant is usually called k<sub>2</sub>. A higher rate constant indicates a faster reaction speed, which means the reaction proceeds more quickly.

In this study, the reaction rate constant K<sub>2</sub> and q<sub>0</sub> of As (V) is 0.006 and 1.55 mg/g & for F is 0.017 and 1.15 mg/g in a single-component system. The pseudo-second-order model fitted the adsorption kinetics much better than the pseudo-first-order and Elovich models for both adsorbates. The pseudo-second-order model assumes that the rate-determining step is chemical adsorption, which is always monolayer adsorption. Thus, the decrease of R<sup>2</sup> with increasing concentration may indicate physical adsorption contributing at higher concentrations, i.e., the formation of more than one layer on the adsorbent surface. The pseudo-second-order model includes all adsorption steps, such as external film (boundary layer) diffusion, internal particle diffusion, and adsorption, which is pseudo-model.

The overall rate of adsorption is controlled by the slowest step (Remena ‘rova’ et al. 2014). Of the three mentioned steps, the third step is assumed rapid, and thus, the slowest step would be either film diffusion or pore diffusion. However, intra-particle and external transport mechanisms might distribute the controlling step.

<table>
<thead>
<tr>
<th></th>
<th>Pseudo-First Order Kinetic Model</th>
<th>q&lt;sub&gt;e&lt;/sub&gt; (mg/g)</th>
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<th>1.13</th>
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<tbody>
<tr>
<td></td>
<td>K (min&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>0.005</td>
<td>0.009</td>
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<tr>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
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<table>
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<th></th>
<th>Pseudo-Second Order Kinetic Model</th>
<th>q&lt;sub&gt;e&lt;/sub&gt; (mg/g)</th>
<th>1.55</th>
<th>1.15</th>
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<tbody>
<tr>
<td></td>
<td>K&lt;sub&gt;2&lt;/sub&gt; (g/(mg.min))</td>
<td>0.006</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.96</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>Intra-particle Diffusion Kinetic Model</th>
<th>K&lt;sub&gt;i&lt;/sub&gt; (mg/g.min&lt;sup&gt;0.5&lt;/sup&gt;)</th>
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<th>0.005</th>
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<td></td>
<td>C&lt;sub&gt;i&lt;/sub&gt;</td>
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<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
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<table>
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<th>Elovich Kinetic Model</th>
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<td></td>
<td>β (g/mg)</td>
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<td>10.63</td>
<td></td>
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<tr>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.95</td>
<td>0.97</td>
<td></td>
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</table>
3.5.2 Kinetics of metal ions for binary component adsorption by activated carbon.

The results of kinetic adsorption studies with the function of contact time for As(V) and F in binary component systems are given in Fig 16a and b. It shows that As(V) adsorption on activated carbon was more than that of fluoride in a binary component system. Initially, the adsorption was slow, then the adsorption process increased up to 24hrs, reaching equilibrium. The co-existence of As(V) and F affects the adsorption rate and reduction in adsorption at time and equilibrium. The kinetic adsorption experiments of As(V) in a binary component system were conducted at V=250 mL, pH = 5, Dosage = 5 g/L, t=25 °C, Co = 10 mg/L at 200 rpm using activated carbon as adsorbent.

Fig. 16. Kinetic adsorption of a) As(V) and b) F in a binary component system

The rate of the chemical reaction is more rapid in the case of fluoride adsorption than in arsenic adsorption. Furthermore, a binary system's reaction rate is faster than a single-component system.

3.6 Isotherm of metal ions for single component adsorption

The adsorption isotherm experiments are conducted with different initial concentrations of 1 to 100 mg/L by adding 5 g/L of activated carbon to 50-100 mL solution in 250 mL conical flasks with pH 5±0.02 at 25±2° C for 48 hours. The pH of the solution was adjusted by adding 0.1N HCl and 0.1N NaOH. Then, the adsorbent is
separated by microfilters. The concentration of arsenic is measured by flame atomic absorption spectrophotometer-Thermo, and the concentration of fluoride is determined by Thermo Orion Ion-Selective Fluoride meter. Isotherm adsorption is studied to determine the maximum adsorption capacity of activated carbon for As (V) and F. The equilibrium data of As(V) & F are better explained by single isotherm models like Langmuir (Eq. 6), Freundlich (Eq. 7), Toth (Eq. 8), Redlich Peterson (Eq. 9) and Modified Langmuir Freundlich (Eq. 10) isotherm models for single-component systems. The results show that activated carbon's adsorption capacity is more significant for As(V) than fluoride in a single-component system with the same experimental conditions.

Fig. 17. Langmuir isotherm model fit of As(V) and F (V=50 mL, t=25 °C, pH = 5, Dosage = 5 g/L, Co = 0.2 to 50 mg/L at 150 rpm using activated carbon as adsorbent)
Fig. 18. Freundlich isotherm model fit of As(V) and F (V=50 mL, t=25 °C, pH = 5, Dosage = 5 g/L, Co = 0.2 to 50 mg/L at 150 rpm using activated carbon as adsorbent)

Fig. 19. Toth isotherm model fit of As(V) and F (V=50 mL, t=25 °C, pH = 5, Dosage = 5 g/L, Co = 0.2 to 50 mg/L at 150 rpm using activated carbon as adsorbent)
Fig. 20. Redlich-Peterson isotherm model fit of As(V) and F (V=50 mL, t=25 °C, pH = 5, Dosage = 5 g/L, Co = 0.2 to 50 mg/L at 150 rpm using activated carbon as adsorbent)

Fig. 21. Modified Langmuir Freundlich isotherm model fit of As(V) and F (V=50 mL, t=25 °C, pH = 5, Dosage = 5 g/L, Co = 0.2 to 50 mg/L at 150 rpm using activated carbon as adsorbent)

Table 2. Equilibrium adsorption isotherm parameters of single component models for As (V) and F by activated carbon.
The experimental adsorption equilibrium data of As(V) and F in single-component systems on activated carbon were analyzed and plotted in Fig 17-21. The calculated correlation coefficients, coefficient of determination ($R^2$), and root mean square errors (RMSE) of five single isotherm models are represented in Table 2. Figure 17 shows the Langmuir isotherm fit with an adsorption capacity of activated carbon was 3.58 and 2.32 mg/g for As(V) and F, respectively. The Langmuir constant of As(V) is 0.036, and for F is 0.11. The adsorption capacity of activated carbon towards As(V) is 1.54 times greater than that of F, indicating activated carbon is more selective for As(V) than for F. Similar results are obtained in the other research by Bibi et al. (2015), and Rathore and Mondal (2017). It was found that the characteristics of the adsorbent and the experimental setup used can impact the system's selectivity sequence of activated carbon. When compared to other adsorbents, activated carbon is shown to have a substantially superior adsorption capacity. Activated carbon is potential material for extracting As(V) and F from water solutions. The comparison of the maximum uptake of As(V) and F with different adsorbents is given in Table 3. The separation factor can determine the nature of adsorption. It is expressed as

<table>
<thead>
<tr>
<th>No</th>
<th>Isotherm Model</th>
<th>Component</th>
<th>Parameters</th>
<th>$R^2$</th>
<th>RMSE</th>
</tr>
</thead>
</table>
| 1  | Two-parameter Langmuir Isotherm Model (LI) | As | $k_L = 0.036$
$Q_m = 3.58 \text{ mg/g}$
$R_L = 0.22$ | 0.97 | 0.37 |
|    |               | F | $k_L = 0.11$
$Q_m = 2.32 \text{ mg/g}$
$R_L = 0.08$ | 0.98 | 0.23 |
| 2  | Freundlich Isotherm Model (FI) | As | $K_F = 0.18$
$n = 1.46$ | 0.94 | 0.49 |
|    |               | F | $K_F = 0.44$
$n = 2.59$ | 0.96 | 0.41 |
| 3  | Three-parameter Toth Isotherm Model (T model) | As | $K_T = 1.16$
$a_T = 16.41$
$t = 1.31$ | 0.97 | 0.38 |
|    |               | F | $K_T = 0.92$
$a_T = 2.16$
$t = 1.25$ | 0.99 | 0.14 |
| 4  | Modified Langmuir Freundlich Isotherm Model (MLF) | As | $k_L = 0.1008$
$Q_m = 2.72 \text{ mg/g}$
$n = 1.81$ | 0.99 | 0.27 |
|    |               | F | $k_L = 0.077$
$Q_m = 2.11 \text{ mg/g}$
$n = 0.71$ | 0.99 | 0.11 |
| 5  | Redlich Peterson Isotherm Model (RPI) | As | $k_RP = 0.11$
$a_{RP} = 0.004$
$\beta = 1.52$ | 0.97 | 0.37 |
|    |               | F | $k_RP = 0.54$
$a_{RP} = 0.51$
$\beta = 0.82$ | 0.99 | 0.12 |
\[ R_L = \frac{1}{1 + K_L C_0} \quad \text{Eq. (12)} \]

\( C_0 \) is the initial concentration, and \( K_L \) is the Langmuir constant of As(V) and F in the solution.

The values of \( R_L \) signify the type of isotherms. It is unfavorable adsorption if the \( R_L \) values exceed 1 (\( R_L > 1 \)). If the values lie between 0 and 1, it’s favorable adsorption; if \( R_L = 0 \), adsorption is irreversible. Hence, \( R_L \) values of As(V) and F onto activated carbon lie between 0 and 1, as shown in Table 2, indicating favorable adsorption (Arup Roy 2013).

Due to its reliability and versatility, the Langmuir isotherm model is widely used in sorption studies. It is beneficial for homogeneous sorption processes and is based on the theoretical concept of monolayer adsorption. This model assumes that the interaction forces between adsorbed molecules are insignificant and that a fixed number of energetically equivalent sites are available on the adsorbent surface. Once an adsorbate molecule occupies a site, no further adsorption occurs. Overall, the Langmuir isotherm model provides a straightforward approach to understanding adsorption phenomena (Al-Ghouti & Da’ana 2020).

Considering higher \( R^2 \) and lowest RMSE values, the Modified Langmuir Freundlich isotherm fits the system more accurately than the other models. Furthermore, the parameter \( n \) is the index of heterogeneity in the MLF model (Eq. 10). When applying a heterogeneity index of \( n \), the density function for heterogeneous systems might change in the MLF isotherm, which usually falls between 0 and 1. A homogeneous material has an \( n \) value of 1, whereas a heterogeneous material has an \( n \) value below 1. In this study, the value of \( n \) is 1.81 and 0.71 for As(V) and F, respectively. In the above equation, the affinity constant \( (K_a) \) value can be varied for pH-dependent sorption effects. The uniqueness of this isotherm is its pH dependency on adsorption systems. The essential experimental condition required to apply this isotherm model in a system is pH (Jeppu & Clement 2012).

Fig. 22. Comparison between predicted uptake with the best model and experimental uptake of arsenic in a
Fig. 23. Comparison between predicted uptake with the best model and experimental uptake of arsenic in a single component system.

Upon examining Figures 22 and 23, the relationship between the predicted uptake of arsenic and fluoride, \(q_{\text{pred}}\), and the experimental uptake, \(q_{\text{exp}}\), was thoroughly investigated to assess the adequacy of the model. The plotted data revealed several straight lines corresponding to the linear graphs associated with the utilized isotherm models. Among the isotherm models considered, namely Langmuir, Freundlich, Modified Langmuir Freundlich, Toth, and Redlich Peterson, it was the Modified Langmuir Freundlich model that displayed the most favorable fit. This model exhibited a higher value of \(R^2\), indicating a stronger correlation between the predicted and experimental data points. Furthermore, the model showed a lower RMSE (Root Mean Square Error) value, which signifies a smaller deviation between the predicted and actual experimental measurements. Based on the experimental data, the Modified Langmuir Freundlich model demonstrated a remarkable ability to predict arsenic and fluoride uptake accurately.

In conclusion, the analysis of Figures 22 and 23 shows that the Modified Langmuir Freundlich model outperformed the other isotherm models by providing the best fit. This finding is supported by its higher \(R^2\) value, lower RMSE error, and capacity to predict the experimental data for arsenic and fluoride reasonably.

### Table 3. Comparison of maximum adsorption capacity for As (V) and F with other adsorbents in binary systems.

<table>
<thead>
<tr>
<th>No</th>
<th>Adsorbent</th>
<th>Adsorbates dosage</th>
<th>Adsorption capacity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>As (mg/L)</td>
<td>F (mg/L)</td>
<td>As (mg/g)</td>
</tr>
<tr>
<td>1</td>
<td>Hydrated Cement (10g/L, 20g/L, 30g/L, 40g/L)</td>
<td>0.1</td>
<td>5</td>
<td>1.92</td>
</tr>
</tbody>
</table>
### 3.7 Isotherm of metal ions for binary component adsorption

The co-existence of arsenic and fluoride in various areas highlights the significance of studying their simultaneous adsorption. This study aimed to investigate the competitive effects of As(V) and F on activated carbon, focusing on their adsorption behavior in a combined system. The presence of F was found to impact the behavior of As(V), which was assessed by considering the interaction mechanism and the maximum uptake of both pollutants in single and binary adsorption systems. By analyzing the interaction mechanisms, it was possible to determine how the presence of F influenced the adsorption behavior of As(V). The study classified the effects of ionic interactions into three categories: synergistic, antagonistic, and no interaction. These classifications helped to understand the combined adsorption behavior of As(V) and F. The study also measured the maximum uptakes of As(V) and F in both single-component and binary adsorption systems. The maximum uptake of As(V) and F in the binary system was denoted as $Q_{\text{maxB}}$, while the maximum uptake in the single-component system was denoted as $Q_{\text{maxS}}$, respectively. If the ratio of $Q_{\text{maxB}}$ and $Q_{\text{maxS}}$ is greater than one, then the mechanism is synergistic. If the ratio is below one, then the effect of the mixture is antagonistic. If the ratio equals one, there is no interaction between the adsorbates in the binary solution (Girish 2019).

\[
\frac{Q_{\text{maxB}}}{Q_{\text{maxS}}} > 1: \text{The combined effect is more significant than the individual effect in the solution.}
\]

\[
\frac{Q_{\text{maxB}}}{Q_{\text{maxS}}} = 1: \text{The solution's combined and individual effects are the same.}
\]

\[
\frac{Q_{\text{maxB}}}{Q_{\text{maxS}}} < 1: \text{The combined effect is less significant than the individual effect in the solution.}
\]

The primary focus of this investigation was to examine the simultaneous adsorption of arsenic and fluoride on activated carbon. The presence of F influenced the adsorption behavior of As(V). Various parameters such as the interaction mechanism, maximum uptake values, additive rule, selectivity ratio, P factor, inhibitory effect, and...
sorption affinity were utilized to gain insights into the combined adsorption behavior of these pollutants in the binary system (Amrutha et al., 2023).

The research also involved studying the binary isotherm adsorption to analyze the maximum adsorption capacity of activated carbon for As(V) and F. The impact of F ion concentrations on the adsorption efficiency of As(V) was examined by varying the F ion concentrations to 10, 20, and 30 mg/L under the same optimized experimental conditions. Similarly, the efficiency of F adsorption was explored by altering the starting concentrations of F ions ranging from 1 to 100 ppm while maintaining a constant level of arsenic.

Competitive isotherm models such as the Extended Langmuir isotherm model and the Extended Freundlich isotherm model were applied to the binary systems. The experiments involved keeping the fluoride concentration constant while varying the starting concentration of arsenic from 1 to 100 ppm. Likewise, studies were conducted with varying fluoride concentrations ranging from 1 to 100 ppm while maintaining a constant level of arsenic.

In summary, this research investigated the simultaneous adsorption of As(V) and F on activated carbon. The presence of F influenced the adsorption behavior of As(V), and various parameters and models were employed to analyze and understand the combined adsorption behavior in the binary system. Additionally, competitive isotherm studies were performed, and the maximum adsorption capacities of activated carbon for As(V) and F were examined under different concentrations and experimental conditions.

3.7.1 Isotherm of metal ions for binary component adsorption with constant fluoride

The binary adsorption system involving various arsenic concentrations and constant fluoride is presented in Fig 22. The experimental conditions included a volume (V) of 100 mL, pH of 5, dosage (adsorbent concentration) of 5 g/L, temperature (t) of 25 °C, and agitation speed of 150 rpm. Activated carbon was utilized as the adsorbent material. The initial concentration of arsenic ranged from 1 to 100 mg/L. At the same time, fluoride concentrations were set at 10, 20, and 30 mg/L. During the competitive isotherm experiments, it was observed that adding fluoride at a constant level of approximately 10 ppm led to a significant reduction in the adsorption of arsenic as As(V).

However, when the fluoride concentration was raised to 20, 30, and higher ppm levels, the ability of arsenic to bind to surfaces was slightly affected. Table 4 provides the parameters, coefficient of determination (R^2), root mean square error (RMSE), and average percentage error (%) for each model used in the analysis. The co-existence of fluoride exhibited various mechanisms, including synergism, antagonism, and non-interaction, as represented in Table 5. Specifically, the presence of fluoride showed antagonistic behavior towards arsenic in this study.

In summary, the investigation focused on a binary adsorption system involving varying concentrations of arsenic and a constant concentration of fluoride. The addition of fluoride had a notable impact on the adsorption behavior of arsenic, with different mechanisms observed based on their co-existence. Table 4 and Table 5 provide detailed information regarding the model parameters, statistical metrics, and the effect of fluoride-arsenic interaction.
Fig. 24. Extended Langmuir isotherm model fit of varying As(V) and constant F at V=100 mL, t=25 °C, pH = 5, Dosage = 5 g/L, Co = 1 to 100 mg/L at 150 rpm using activated carbon as adsorbent

Table 4. Equilibrium adsorption isotherm parameters of competitive model Extended Langmuir isotherm model for varying As(V) with constant F by activated carbon.

<table>
<thead>
<tr>
<th>No</th>
<th>Isotherm Model</th>
<th>Concentrations (mg/L)</th>
<th>Parameters</th>
<th>R²</th>
<th>APE (%)</th>
<th>RMSE</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Extended Langmuir Isotherm Model (EL)</td>
<td>5 to 100</td>
<td>( k_L = 0.036 ) [\text{mg/g} ] ( Q_m = 3.54 \text{ mg/g} )</td>
<td>0.97</td>
<td>3.92</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>( k_L = 0.0829 ) [\text{mg/g} ] ( Q_m = 2.35 \text{ mg/g} )</td>
<td>0.97</td>
<td>4.22</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>( k_L = 0.0756 ) [\text{mg/g} ] ( Q_m = 2.20 \text{ mg/g} )</td>
<td>0.96</td>
<td>4.32</td>
<td>4.87</td>
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<tr>
<td></td>
<td></td>
<td>30</td>
<td>( k_L = 0.0851 ) [\text{mg/g} ] ( Q_m = 2.21 \text{ mg/g} )</td>
<td>0.98</td>
<td>2.34</td>
<td>1.62</td>
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Table 5. The effect of ionic interactions of varying As(V) and constant F

<table>
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<tr>
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<th>Isotherm Model</th>
<th>Concentrations (mg/L)</th>
<th>Maximum uptake (mg/g)</th>
<th>Ratio = ( Q_{maxB}/Q_{maxS} )</th>
<th>Interaction mechanism</th>
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<tr>
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<td>-</td>
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<td></td>
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<td>2.20</td>
<td>0.62</td>
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<td></td>
<td>30</td>
<td>2.21</td>
<td>0.62</td>
<td>Antagonistic</td>
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</tbody>
</table>
3.7.2 Isotherm of metal ions for binary component adsorption with constant arsenic

The binary adsorption system with various fluoride concentrations and constant arsenic is illustrated in Fig 23. The experimental conditions involved a volume (V) of 100 mL, pH of 5, dosage (adsorbent concentration) of 5 g/L, temperature (t) of 25 °C, and agitation speed of 150 rpm. Activated carbon was employed as the adsorbent material. The initial concentration of fluoride ranged from 1 to 100 mg/L, while the concentrations of arsenic were set at 10, 20, and 30 mg/L. The competitive isotherm experiments revealed a notable decrease in fluoride adsorption upon adding approximately 10 ppm of arsenic. However, as the concentration of arsenic was raised to 20, 30, and higher ppm levels, the ability of fluoride to bind to surfaces was less affected. In this study, Table 6 presents the parameters, coefficient of determination (R²), root mean square error (RMSE), and average percentage error (%) for each model used in the analysis. The co-existence of arsenic demonstrated different mechanisms, including synergism, antagonism, and non-interaction, as shown in Table 7. In this case, fluoride exhibited an antagonistic behavior when arsenic was present.

In summary, the study investigated the competitive adsorption of fluoride and arsenic in a binary system. The concentration of arsenic affected the adsorption behavior of fluoride, with a significant impact observed at around 10 ppm of arsenic. However, higher concentrations of arsenic had a comparatively lesser effect on fluoride uptake.

![Fig 25. Extended Langmuir isotherm model fit of varying F and constant arsenic (V=100 mL, t=25 °C, pH = 5, Dosage = 5 g/L, Co = 1 to 100 mg/L at 150 rpm using activated carbon as adsorbent)](image)

<table>
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<tr>
<th>No</th>
<th>Isotherm</th>
<th>Concentrations (mg/L)</th>
<th>Parameters</th>
<th>R²</th>
<th>APE</th>
<th>RMSE</th>
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Table 6. Equilibrium adsorption isotherm parameters of competitive model Extended Langmuir isotherm model for varying As(V) with constant F by activated carbon.
<table>
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<th>Model</th>
<th>F</th>
<th>As(V)</th>
<th>$k_L$</th>
<th>$Q_m$</th>
<th>$Q_{maxB}/Q_{maxS}$</th>
<th>Interaction mechanism</th>
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<td>1</td>
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<td>0.1308</td>
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<td>0.97</td>
<td>3.27</td>
<td>0.21</td>
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</table>

Table 7. The effect of ionic interactions of varying F and constant As(V)

<table>
<thead>
<tr>
<th>No</th>
<th>Isotherm Model</th>
<th>Concentrations (mg/L)</th>
<th>Maximum uptake (mg/g)</th>
<th>$Q_{maxB}/Q_{maxS}$</th>
<th>Interaction mechanism</th>
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<td>-</td>
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<td></td>
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<td>2.00</td>
<td>0.86</td>
<td>Antagonistic</td>
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<td></td>
<td>20</td>
<td>2.05</td>
<td>0.88</td>
<td>Antagonistic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>1.98</td>
<td>0.85</td>
<td>Antagonistic</td>
</tr>
</tbody>
</table>

Table 8. Ionic properties of As(V) and F

<table>
<thead>
<tr>
<th>No</th>
<th>Properties</th>
<th>As(V)</th>
<th>F</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydrated radii (Å)</td>
<td>&gt;2-2.2</td>
<td>3.52</td>
<td>(Padilla &amp; Saitua 2010; Saitua et al. 2011)</td>
</tr>
<tr>
<td>2</td>
<td>Ionic radii (Å)</td>
<td>0.39</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Electronegativity (Pauling)</td>
<td>2.18</td>
<td>3.98</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ion diffusivity (10&lt;sup&gt;-9&lt;/sup&gt; m²/S)</td>
<td>0.323</td>
<td>1.46</td>
<td></td>
</tr>
</tbody>
</table>

The extended Langmuir and extended Freundlich parameters for fluoride and arsenic in binary adsorption studies are provided in Tables 4 and 6, respectively. The results indicate that when competitive ions of fluoride increase, the removal capacity of arsenic decreases, and vice versa. It is observed that the adsorption performances are slightly lower in binary systems compared to single systems. This can be attributed to the competition between ions to access the active sites on the adsorbent and the affinity of the ions towards the activated carbon. The specific properties and behavior of the ions in the binary system are also considered, including electronegativity, hydrated radii, ion diffusivity, suitable site properties for uptake, and the formation of hydroxyl complexes (as shown in Table 8) (Arup Roy 2013; Şahan 2019).

One significant factor influencing competitive adsorption is the hydrated radii. The hydrated radii of As(V) are in the range of 2-2.2 Å, while for F, it is 3.52 Å. Higher hydrated radii indicate lower accessibility to the surface and...
pores of activated carbon. Consequently, As(V) adsors more rapidly than fluoride in simultaneous adsorption. The affinity and suitability of As(V) and F for activated carbon also contribute to the competition between the ions in the solution. However, the maximum uptake of arsenic is observed to be higher than that of fluoride. The equilibrium adsorption capacity follows the order As(V) > F in simultaneous adsorption. When the fluoride concentration increases in an arsenic solution, fluoride has a slight impact on the uptake of arsenic. Similarly, when the arsenic concentration increases in a fluoride solution, arsenic affects the fluoride uptake.

4. CONCLUSION

This study investigates activated carbon’s characterization and adsorption behavior as an adsorbent. In single-component systems, activated carbon demonstrates efficient adsorption of arsenic and fluoride, achieving a percentage removal of 93.56% for arsenic and 72% for fluoride. Similarly, in binary-component systems, the percentage removal of As(V) is found to be 71.91%, while fluoride is removed at a rate of 90%. Additionally, experimental data for arsenic and fluoride adsorption using activated carbon indicate that maximum adsorption occurs at pH 3. The adsorption rate of As(V) and fluoride decreases with increasing solution pH, possibly due to the negatively charged surface of the adsorbent at higher pH levels. Similarly, in a binary system, As(V) and fluoride exhibit a significant decrease in adsorption as pH increases.

The pseudo-second-order equation best describes the adsorption process, as evidenced by a coefficient of determination (R²) approaching 1 and linearity observed in the t/qt vs. t plot. The reaction rate constants (K₂) for As(V) and fluoride in single-component systems are determined as 0.006 and 0.017, respectively, suggesting a faster reaction rate for fluoride adsorption than arsenic.

In the single-component system, the maximum uptake for fluoride is 2.32 mg/g, while for arsenic is 3.58 mg/g. Also, the Modified Langmuir Freundlich isotherm model showed the best fit for As(V) and F in a single-component system with higher R² and lower RMSE. In a simultaneous system, the presence of fluoride exhibits antagonistic behavior on the co-existence of arsenic, resulting in a decrease in the maximum uptake of arsenic in the binary adsorption system. Specifically, with a co-existence of 10 mg/L fluoride, the maximum uptake of arsenic is reduced to 2.35 mg/g, and at 20 mg/L fluoride, it further decreases to 2.20 mg/g. Thus, the results demonstrated that the uptake of As(V) is significantly affected by the interference of fluoride. These findings have implication in arsenic and fluoride adsorption in groundwater.
Statements and Declarations

Ethical Approval
The authors declare that ethical considerations have been taken care of while writing the manuscript.

Consent to Participate
The experimental paper does not involve human subjects.

Consent to Publish
We declare that there is no conflict of interest associated with this manuscript. As the corresponding author, we confirm that the manuscript has been proofread and approved for submission by all named authors.

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Chikmagalur Raju Girish: Project administration, Validation, Resources, Supervision, review, and editing.
Balakrishna Prabhu: Project administration, Validation, Resources, Supervision, review and editing.
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Competing Interests
The authors declare that there is no conflict of interest associated with this work, and the manuscript has been approved for submission by all named authors.

Availability of data and materials
All the data can be provided to the editorial team upon request.


Arup Roy JB (2013) A binary and ternary adsorption study of wastewater Cd(II), Ni(II) and Co(II) by c-Fe2O3 nanotubes Elsevier. https://doi.org/https://doi.org/10.1016/j.seppur.2013.05.010


Kumar A, and Jena HM (2016) Preparation and characterization of high surface area activated carbon from Fox nut (Euryale ferox) shell by chemical activation with H3PO4. Results in Physics, 6, 651–658. https://doi.org/10.1016/j.rinp.2016.09.012


Merrikhpour H, and Jalali M (2013) Comparative and competitive adsorption of cadmium, copper, nickel, and
lead ions by Iranian natural zeolite. Clean Technologies and Environmental Policy, 15(2), 303–316.
https://doi.org/10.1007/s10098-012-0522-1


https://doi.org/10.21577/0103-5053.20190138

https://doi.org/10.1186/s40543-020-0206-0


https://doi.org/10.1016/j.desal.2010.03.022


https://doi.org/10.1016/j.jece.2016.04.017

https://doi.org/10.1021/acs.iecr.7b01139

https://doi.org/10.1016/j.jenvman.2017.05.081

https://doi.org/10.1007/s11270-020-04610-1

https://doi.org/10.1016/j.jwpe.2019.100867
 zirconium modified activated carbon derived from chemical carbonization of Tectona grandis sawdust:
 Isotherm, kinetic, thermodynamic and breakthrough curve modelling. Environmental Research,

 and fluoride from aqueous solution by biomass based activated biochar: Optimization through response
 https://doi.org/10.1016/j.jece.2017.10.027

 plant from naturally contaminated groundwater. Desalination, 274(1–3), 1–6.
 https://doi.org/10.1016/j.desal.2011.02.044

Salih SS, Mohammed HN, Abdullah GH, Kadhom M, and Ghosh TK (2020) Simultaneous Removal of Cu(II),
 Cd(II), and Industrial Dye onto a Composite Chitosan Biosorbent. Journal of Polymers and the

 https://doi.org/10.1016/j.jhazmat.2010.09.001

 https://doi.org/10.1016/j.cej.2014.03.118

Xiang Y, Xu H, Li C fu, Demissie H, Li K, and Fan H (2022) Effects and behaviors of Microcystis aeruginosa in
 defluorination by two Al-based coagulants, AlCl3 and Al13. Chemosphere, 286(P3), 131865.
 https://doi.org/10.1016/j.chemosphere.2021.131865

Xu YH, Nakajima T, and Ohki A (2002) Adsorption and removal of arsenic(V) from drinking water by aluminum-

 hierarchically porous carbons. Journal of the Taiwan Institute of Chemical Engineers, 93, 543–553.
 https://doi.org/10.1016/j.tjite.2018.08.038

 https://doi.org/10.1016/j.jhazmat.2019.05.060