

Isotherm and kinetic modelling for assessing the effectiveness of economical adsorbents in sewage water treatment

Ayushi Jha^{1*}, Sunil Garg¹, Sanjay Satpute¹, Jagdish Prasad Singh¹, Dhanwinder Singh², Urmila Gupta Phutela³,
Manojit Chowdhury⁴ & Derminder Singh⁵

¹Department of Soil and Water Engineering, ²Department of Soil Science, ³Department of Renewable Energy Engineering, & ⁵Department of Electrical Engineering and Information Technology, Punjab Agricultural University, Ludhiana-141004, Punjab, India

⁴Division of Agricultural Engineering, ICAR-Indian Agricultural Research Institute, New Delhi, India

*E-mail: ayushi-2031002@pau.edu/ayushijhagsm@gmail.com

Received 18 October 2023; accepted 23 February 2024

In the face of growing environmental challenges and the urgent need for sustainable solutions, this research delves into an innovative approach to wastewater treatment by harnessing the power of agricultural waste materials as efficient adsorbents. The focuses on mitigating water pollution and bringing irrigation water quality in line with strict maximum permissible limits (MPLs). Initial assessments revealed elevated levels of contaminants, all exceeding MPLs. Among ten adsorbent materials tested, Rice Husk Ash (RHA), Sugarcane Bagasse (SB), and Ferric Oxide Sand (Fe-S), emerged as highly effective materials, achieving maximum reductions. Optimized conditions for adsorbent dosage, contact time, and wastewater load were identified which was 2.0 g of adsorbent, 250 mL of sewage water load at 15 min contact time. RHA demonstrated a remarkable 60-75% reduction in BOD, 52-67% in COD, and over 100% in RSC reduction. SB achieved reductions of 57-67% in BOD, 47-59% in COD, and 41-76% in RSC. Fe-S delivered significant reductions in COD (51-61%) and nearly 100% in RSC reduction. Kinetic studies confirmed pseudo-second-order kinetics as the dominant adsorption mechanism, with correlation coefficients (R^2) exceeding 0.98, further supporting the effectiveness of these adsorbents. This research underscores the potential of agricultural waste-based adsorbents, especially RHA and SB, in treating sewage water pollutants and making it fit for irrigation.

Keywords: Agricultural waste, Adsorbents, Batch studies, Kinetic and isotherm models, Sewage water treatment

Introduction

Water availability is vital for sustaining livelihoods and ensuring the well-being of all living organisms. It plays a fundamental role in various essential activities, such as agriculture, industry, and domestic use. Adequate access to clean and safe water is not only necessary for meeting basic human needs but also for promoting overall health, sanitation, and economic development^{1,2}. In the present era, a significant environmental concern confronting humanity is the escalating global pollution of freshwater systems caused by a multitude of organic and inorganic compounds. Domestic and industrial wastes are primary contributors to water body pollution, collectively generating approximately 72,368 million liters per day (MLD) of sewage in urban areas³.

The limited availability of fresh water, particularly in the major water consuming sector of agriculture, underscores the urgent need to explore alternative water sources. Therefore, the importance of wastewater treatment is escalating, due to the depletion of water resources, rising costs associated with wastewater

disposal, and increasingly stringent regulations on discharge^{4,5}. These regulations have lowered the acceptable levels of contaminants in waste streams, necessitating more effective and efficient treatment processes. The water pollutants are diverse in nature; this creates a variety of water treatment methods that are not only effective but also technologically and economically viable.

Many researchers have explored various methods for wastewater treatment, including chemical precipitation, membrane filtration, ion exchange^{6,7} and adsorption. Among these options, adsorption stands out as a preferred choice due to its flexibility, cost-effectiveness, efficiency, and environmentally friendly. In adsorption, specific substances are selectively moved from the liquid phase and attached to a solid adsorbent material's surface^{8,9}. This process involves complex interactions among three main components: the adsorbent material, the substances being removed (adsorbate), and the wastewater itself. Selecting the right adsorbent material adds an extra layer of complexity, as it should have features like a large

surface area, porosity, stability against environmental factors, affordability, and suitable physical and chemical properties, all while avoiding the production of harmful substances¹⁰.

A batch experiment involves mixing a fixed amount of adsorbent with contaminated solution to evaluate how well the adsorbent removes contaminants. Factors like adsorbent quantity, contact time, pH, temperature, and initial contaminant levels to understand the adsorption process and optimize water treatment methods¹¹. These studies help fit kinetic models, revealing the rate and mechanisms of contaminant removal. Kinetic models explain how quickly adsorption occurs. Additionally, batch experiments aid in fitting isotherm models like Langmuir or Freundlich, determining maximum adsorption capacity and energy. Isotherm models describe the equilibrium relationship between adsorbent and wastewater concentrations, offering insights into capacity and affinity. Together, batch studies and models optimize adsorbent selection for wastewater treatment¹².

Many studies have explored the use of adsorption-based methods for wastewater treatment, employing various adsorbent materials^{13,14,8,9,15,4,16}. However, there remains a significant research gap in comprehensively employing multiple adsorbent materials to simultaneously target a range of contaminants within acceptable limits for irrigation water use. This study aims to address this gap by carefully selecting materials through batch studies and applying various adsorption-based models. The objective is to provide an environmentally sustainable and economically feasible approach to wastewater treatment.

Experimental Section

Study area

The experiment was conducted at the Department of Soil and Water Engineering, Punjab Agricultural University (PAU), Ludhiana, Punjab, India. Ludhiana is situated at 30° 53' N and 74° 49' E, with an elevation of 247 m above sea level. The climate in Ludhiana is characterized as subtropical and semi-arid. The sewage water sample for testing was collected from an aerated pond within the university campus of Punjab Agricultural University, Ludhiana, Punjab, India.

Collection and testing of sewage water samples

Sewage water samples were collected twice a week for duration of approximately six months. These

collected samples were subjected to testing for various parameters, including Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Ammonium Nitrogen (NH₄-N) and Nitrate Nitrogen (NO₃-N), and Residual Sodium Carbonate (RSC), in order to obtain a range of values. The results of both the pre-testing and post-testing of the samples were recorded.

Collection and preparation of adsorbent materials

The main objective of the study was to utilize agricultural waste as a cost-effective adsorbent material. Various materials, including rice husk (RH), rice husk ash (RHA), sugarcane bagasse (SB), sugarcane bagasse ash (SBA), corn cob (CC), groundnut shell (GS), charcoal (CH), briquettes (BR) were investigated for their potential applications in wastewater treatment. Furthermore, a laboratory-scale preparation of Ferric oxide sand (Fe-S) was undertaken. Given its abundant pores and strong adsorbent properties¹⁷, Fe-S holds potential as a distinct layer in future sewage treatment systems. This layer could enhance the overall treatment process and system efficiency. Therefore, following the chemical treatment of sand and the creation of ferric oxide sand, we conducted tests to evaluate its removal efficiency, alongside other adsorbents. The adsorbent materials underwent a series of steps for preparation. First, they were thoroughly washed to eliminate impurities and foreign substances. Subsequently, they were sun dried and further dried in an oven to remove excess moisture. The dried adsorbent materials were then ground to achieve a specific size and passed through different sieves. Rice husk ash was sieved to a size of 10 micron, the bagasse was ground and sieved to a 0.5 mm size and Ferric oxide coated sand was sieved to 1.0 mm size. Finally, the prepared adsorbent material was carefully collected in airtight bottles to maintain its quality and integrity.

Preparation of Ferric oxide sand

Ferric oxide sand was prepared in the laboratory for which sand was collected from the construction site where excess sand was generated. Then it was washed thoroughly using distilled water to remove the excess of impurities. Sand was soaked in sulphuric acid in the ratio of 2:1 (Sand: H₂SO₄) for 24 h. After 24 h, the acid soaked sand was washed with de-ionized water until the runoff was clear and pH of water becomes neutral (7.0). After washing, the sand was put in the oven for drying. Ferric chloride (FeCl₃) was used for the iron

oxide coating and 10 molarity sodium hydroxide (NaOH) was used for making solution basic. 80 mL of 2.47 molarity solution of ferric chloride was added to washed and dried sand and the pH was adjusted to 11.0 by adding 2 mL of NaOH solution and mixed for 2 min. Further, to prepare iron oxide coated sand, process that is followed is depicted in Fig. 1.

Preparation of ferric chloride solution

Ferric chloride solution was used during the entire coating procedure. The molecular weight of ferric chloride is 162.2. The desired solution of 2.47 molarity was prepared by dissolving 40.06 g of ferric chloride in 100 mL distilled water. The desired weight of FeCl_3 was obtained using Eq. 1.

$$\text{Weight (g/L)} = \text{Molecular weight} \times \text{Molarity of Solution} \dots (1)$$

Preparation of sodium hydroxide solution:

Sodium hydroxide was utilized to establish an alkaline solution. This 10 M NaOH solution was formulated by dissolving 4 g of NaOH in 10 mL of distilled water. The requisite quantity of NaOH was determined through the use of Eq. 1, thus facilitating the preparation of the 10 M solution.

Wastewater quality parameters

The focus of the study was to reduce the levels of various parameters, including BOD, COD, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and RSC to meet the maximum permissible limits (MPL) for the purpose of irrigation. The specific permissible limits for each parameter may vary depending on the irrigation method and local regulations. Before conducting the adsorption experiments, the wastewater samples were tested for quality parameters mentioned below.

Biochemical Oxygen Demand (BOD)

It measures the amount of dissolved oxygen required by microorganisms to decompose organic matter in the water. High BOD levels indicate high organic pollution. The BOD was determined by measuring the oxygen depletion in a sealed bottle over a specific incubation period and the process is described in Fig. 2.

Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) measures the amount of oxygen required to oxidize both organic and inorganic substances in water, providing an indication of pollution levels. This parameter was assessed using chemical oxidation methods, which

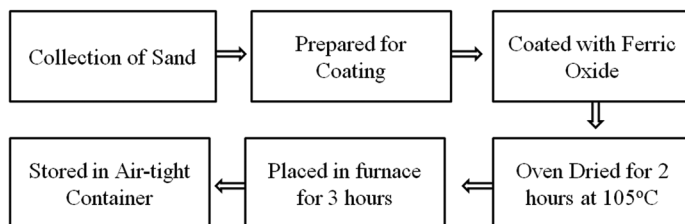


Fig. 1 — Flow chart depicting process of Ferric oxide sand preparation

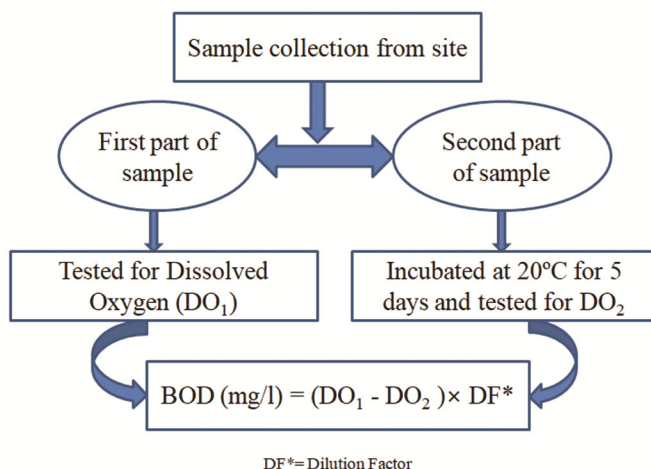


Fig. 2 — Flow chart depicting the process of BOD estimation

determine the oxygen demand of both organic and inorganic compounds (Fig. 3).

Residual sodium Carbonate (RSC)

It is a measure of the water's potential to cause sodicity and can impact soil quality. The RSC can be calculated using the concentration of ions, such as carbonate, bicarbonate, calcium and magnesium. Versenate method was used for calcium and magnesium determination. Carbonate and bicarbonate ions in the sample were computed by titration (Fig. 4).

Ammonium Nitrogen (NH₄-N) and Nitrate Nitrogen (NO₃-N)

They are indicators of nitrogen pollution in the water. The MPL for these nitrogen parameters in irrigation water depends on the specific crop and its nutrient requirements. The levels of ammonium nitrogen and nitrate nitrogen were determined using steam distillation methods. The process has been shown in Fig. 5.

Batch adsorption experiment

In the batch adsorption experiment, key factors such as contact time, adsorbent dose, and wastewater load were investigated at a constant shaking speed to assess their impact on the process. Fig. 6 illustrates the steps involved in the batch experiment, while Table 1 provides an overview of the experimental plan.

Selection of adsorbent dose

The study tested varying doses of the adsorbent, ranging from 1.25 to 2.0 g, to determine the optimum quantity. Different amounts of wastewater, including

150, 250, and 500 mL, were added to assess the effects of different loadings. The experiments were conducted under a fixed contact time of 15 min. Each flask contained a predetermined amount of various adsorbents along with a fixed quantity of the wastewater sample at a time. The flasks were then placed on an orbital shaker and set to shake at a constant speed of 150 rpm for 15 min.

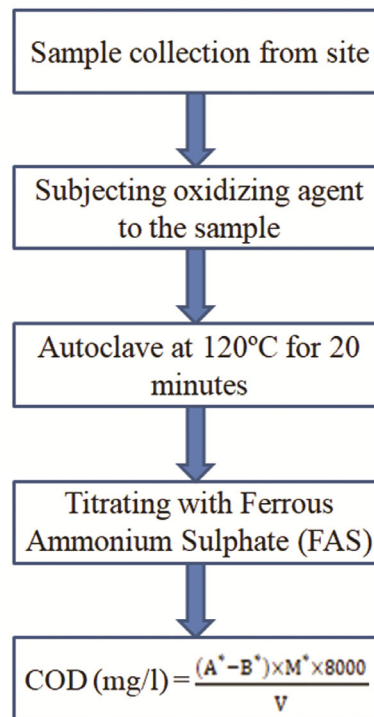


Fig. 3 — Flowchart showing the estimation process of COD

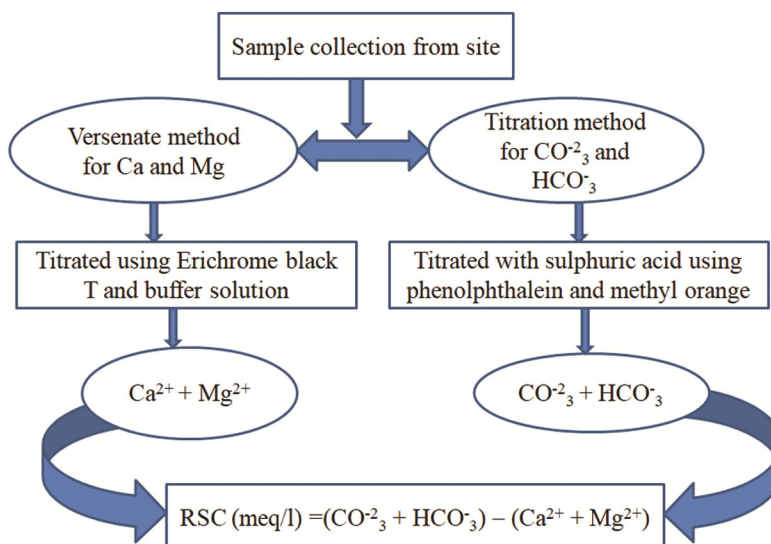


Fig. 4 — Flow chart depicting the process of RSC estimation

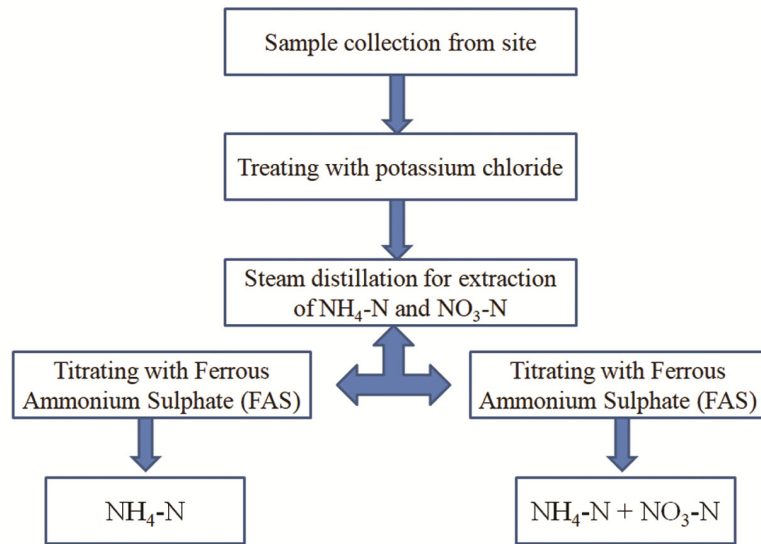


Fig. 5 — Flow chart depicting the process of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ estimation



Fig. 6 — Layout illustrating step-by-step progression of the batch experiment

Table 1 — Experimental plan

Independent parameters	Values
Adsorbent dose (g)	1.25, 1.5, 1.75, 2.0
Contact time (min)	5, 10, 15
Wastewater load (mL)	150, 250, 500
Dependent parameters	
BOD	Percentage removal
COD	Percentage removal
RSC	Percentage removal
NH ₄ -N and NO ₃ -N	Percentage removal

Determination of ideal contact time

The determination of the optimum contact time involved placing the optimized amount of different adsorbents in shaking flasks. Subsequently, wastewater was added to each flask, and the mixtures were shaken for 5, 10, and 15 min, respectively. After the specified shaking duration, the solutions were filtered, and the absorbances of the respective samples were measured in terms of percentage removal and the contact time giving maximum percentage removal is selected.

Determination of ideal wastewater load

The optimization of the wastewater was performed by adding 150, 200 and 500 mL wastewater sample placed with optimized amount of adsorbent material for optimized contact time. After the specified shaking duration, the solutions were filtered, and the absorbance of the respective samples were measured in terms of percentage removal and the contact time giving maximum percentage removal is selected.

Adsorption capacity

The calculation of the adsorption capacity, represented as q_e (mol/g), was performed using the mass balance equation (Eq. 1)

$$q_e = \frac{(C_0 - C_t)V}{W} \quad \dots (1)$$

Furthermore, the percentage removal or reduction in pollutants using different adsorbents was determined using the following presented in Eq. 2

$$\% \text{ Removal} = \frac{(C_0 - C_t)100}{C_0} \quad \dots (2)$$

In the Eq. 1 and 2, C_0 represents the initial concentration (mg/L), C_t is the concentration after treatment (mg/L), V is the volume of the solution in milliliters (mL), and W is the mass of the dry adsorbent used in grams (g).

On the basis of removal efficiency, out of several available adsorbent material, material with maximum

removal efficiency were selected for further kinetic and isotherm studies.

Adsorption kinetics

Kinetic study was conducted with the selected dosage of adsorbents and wastewater load. The samples were shaken at an agitation rate of 150 rpm. The samples were taken out at 15, 30, 60, 120, 180, 300, 540 and 720 min and adsorption rates of COD, BOD and RSC were studied. The modeling of the adsorption kinetics was checked by two common models, pseudo first-order and pseudo-second-order. The pseudo-first order kinetics assumes that the rate of adsorption is directly proportional to the difference between the initial concentration and the concentration at any given time during the adsorption process. In this model, the plot of $\ln(q_e - q_t)$ against time should yield a linear relationship if the adsorption process follows pseudo-first order kinetics.

It can be mathematically represented as Eq. 3

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

Where, q_e is the amount of adsorbate adsorbed at equilibrium, q_t is the amount of adsorbate adsorbed at time t and k_1 is pseudo-first order rate constant

The pseudo-second order kinetics suggests that the rate of adsorption is proportional to the square of the concentration difference between the initial concentration and the concentration at any given time. In this model, plotting t/q_t against time should result in a linear relationship if the adsorption process follows pseudo-second order kinetics. The equation for the pseudo-second order kinetics represented as Eq. 4

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

Where, k_2 is the pseudo-second order rate constant

Adsorption isotherms

In this study, Langmuir and Freundlich isotherm models were considered for adsorption analysis. In its linear form, the Langmuir equation (Eq. 5), describes the adsorption process and the formation of a monolayer on the surface of the adsorbent. On the other hand, the Freundlich model is another widely used adsorption isotherm. In its logarithmic form, it refers to the Freundlich equation (Eq. 6), which describes the adsorption process for heterogeneous surfaces and multilayer adsorption.

$$\frac{1}{q_e} = \frac{1}{k_1 q_m} \cdot \frac{1}{C_e} + \frac{1}{q_m} \quad \dots (5)$$

Where, C_e and q_e represent the concentrations of COD, BOD, and RSC at equilibrium (mg/L) in solution and in solid phase, respectively. q_m is the maximum monolayer adsorption capacity (mg/g) and k_1 is the Langmuir constant which indicates the adsorption energy (L/mg). The values of q_m and k_1 can be determined from the linear plot of C_e/q_e versus C_e

$$\ln q_e = \ln C_e \cdot \frac{1}{n} + \ln k_f \quad \dots (6)$$

A plot of $\ln q_e$ vs. $\ln C_e$ will yield a straight line of slope $\ln k_f$ and intercept $1/n$. Knowing values for slope and intercept allows to easily calculating values of two parameters k_f and n .

Result and Discussion

Initial assessment wastewater quality parameters

The initial values of various wastewater quality parameters, including BOD, COD, RSC, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ are presented in Table 2. The values of parameters were determined in laboratory, such that BOD value ranges from 100 to 150 mg/L, value of COD was ranging from 80-100 mg/l, RSC showed the value range of 2.3-3.0 mg/L, whereas $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ showed the value in the range of 4.8-5.4 ppm and 5-10 ppm respectively. The results showed that, parameters exceeded the maximum permissible limits for irrigation water (Table 2). High BOD and COD in sewage result from abundant organic matter and

pollutants from human activities, including waste, chemicals, and industry.

High BOD and COD levels in sewage water are typically attributed to the presence of organic matter from sources such as human waste, household chemicals, and industrial effluents, which contribute to the overall organic load in wastewater. The higher residual sodium carbonate (RSC) in sewage may be due to the presence of dissolved bicarbonate and carbonate ions, which can contribute to water hardness. The elevated levels of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in sewage water are typically due to the decomposition of organic nitrogen compounds and the incomplete removal of these compounds during wastewater treatment processes.

Batch adsorption experiment

In the batch study, a total of 10 adsorbent materials were examined, namely RH, RHA, SB, SBA, CC, GS, CHAR, BR, and Fe-S. Among these materials, four material viz. RHA, SBA and Fe-S demonstrated the highest percentage reduction in BOD, COD, RSC, $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, and as presented in Table 3.

Table 2 — Initial water quality parameter value (Decree of Ministry for the Environment, 2006)

Water quality parameters	Initial range	MPL for irrigation
BOD (mg/L)	100-150 mg/L	20
COD (mg/L)	120-150 mg/L	100
RSC (me/L)	2.3-3.0 me/L	≤2.25
$\text{NO}_3\text{-N}$ (ppm)	4.8-5.4 ppm	1.5
$\text{NH}_4\text{-N}$ (ppm)	5-10 ppm	2

Table 3 — Percentage reductions of BOD, COD, RSC, $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ under varied adsorbent dosage, contact time and sample amount for different adsorbent materials

Adsorbents	Water quality parameters	Percentage reduction									
		Adsorbent dose (g)				Contact time (min)			Sample amount (mL)		
RH		1.25	1.5	1.75	2.0	5	10	15	150	250	350
	COD	44.72	46.24	49.92	51.92	38.91	44.02	43.99	44.71	51.2	50.31
	BOD	40.98	43.61	45.25	47.54	34.86	39.94	41.47	41.35	46.70	45.81
	RSC	11.54	15.57	19.23	23.08	37.91	46.17	48.06	12.76	20.89	18.97
	$\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$	25.67	29.45	35.89	40.01	25.07	30.15	31.23	27.63	39.21	33.23
RHA		1.25	1.5	1.75	2.0	5	10	15	150	250	350
	BOD	60.68	66.25	72.96	75.68	59.23	69.21	70.53	65.28	72.93	70.15
	COD	52.33	56.16	60.33	67.58	52.97	59.04	59.81	55.42	63.97	60.19
	RSC	138.7	140.01	146.15	180.76	100.03	129.05	130.07	126.84	149.31	136.62
	$\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$	37.82	41.16	45.29	52.73	35.08	44.04	44.83	41.73	48.29	45.51
SB		1.25	1.5	1.75	2.0	5	10	15	150	250	350
	BOD	57.16	58.91	64.15	66.78	55.21	62.73	63.41	65.12	72.58	69.35
	COD	47.83	51.04	56.43	59.22	46.33	54.95	55.62	54.26	62.79	58.53
	RSC	37.84	49.27	57.91	63.55	41.85	76.56	79.13	126.84	133.31	130.07
	$\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$	38.57	40.82	43.19	46.63	31.96	40.53	42.25	41.59	49.05	35.82

(Contd.)

Table 3 — Percentage reductions of BOD, COD, RSC,NO₃-N and NH₄-N under varied adsorbent dosage, contact time and sample amount for different adsorbent materials — (Contd.)

Adsorbents		Percentage reduction									
	Water quality parameters	Adsorbent dose (g)				Contact time (min)			Sample amount (mL)		
		1.25	1.5	1.75	2.0	5	10	15	150	250	350
SBA	BOD	37.48	42.74	44.37	46.15	31.23	40.51	41.03	40.23	42.93	41.58
	COD	25.61	28.50	32.24	34.21	25.12	29.51	30.02	29.42	34.79	31.79
	RSC	11.36	13.79	15.42	18.05	10.30	14.72	15.02	13.56	19.68	16.12
	NO ₃ -N and NH ₄ -N	16.73	18.41	20.06	23.17	15.20	19.63	20.09	16.24	20.06	18.15
CHAR	BOD	60.28	63.93	67.08	70.74	31.23	40.53	41.50	61.84	68.30	65.07
	COD	35.47	35.89	39.37	45.37	25.14	29.52	30.01	43.17	42.24	41.31
	RSC	21.63	24.17	28.45	32.82	10.36	14.74	15.03	23.56	28.90	26.23
	NO ₃ -N and NH ₄ -N	28.65	30.28	34.12	37.79	15.24	19.46	20.04	30.82	35.28	33.05
SA	BOD	63.96	67.71	70.41	73.62	63.81	69.12	70.92	65.82	70.26	68.04
	COD	46.94	50.82	55.76	61.76	45.7	52.11	54.09	49.95	56.39	53.17
	RSC	98.23	105.57	113.94	147.12	90.51	96.80	99.07	100.89	109.35	105.12
	NO ₃ -N and NH ₄ -N	36.84	39.27	42.13	46.55	35.92	41.21	44.18	36.23	42.67	30.45
PS	COD	37.89	41.70	43.85	47.13	35.23	40.57	42.98	40.78	45.30	43.04
	BOD	32.95	33.81	37.90	40.29	30.12	35.25	36.84	31.62	36.40	34.01
	RSC	16.83	18.57	21.29	25.12	15.68	18.21	19.45	15.93	20.60	18.27
	NO ₃ -N and NH ₄ -N	12.78	13.78	17.89	26.89	13.87	16.53	18.79	13.98	20.68	17.33
CC	COD	31.68	33.96	34.55	40.30	30.28	33.49	34.71	32.84	37.20	35.02
	BOD	28.76	32.98	34.35	39.91	28.43	31.57	33.69	31.87	36.17	34.02
	RSC	12.36	14.79	17.42	19.85	10.92	12.64	14.39	14.72	19.10	16.91
	NO ₃ -N and NH ₄ -N	17.82	19.13	21.57	23.94	17.35	19.17	20.98	19.47	23.85	21.66
GS	COD	35.94	39.89	42.67	47.76	35.72	38.09	40.41	33.94	44.08	41.01
	BOD	25.13	27.56	32.94	36.72	26.33	28.79	31.12	26.73	34.87	32.80
	RSC	13.42	15.16	16.93	18.78	11.94	13.68	15.42	14.61	18.81	16.71
	NO ₃ -N and NH ₄ -N	17.92	20.13	24.57	28.81	15.23	19.57	23.91	17.53	25.69	23.61
BR	COD	25.24	28.47	34.35	37.02	22.57	28.14	33.71	25.83	34.23	32.03
	BOD	25.00	26.46	29.77	31.67	20.62	26.31	31.99	26.57	30.69	28.63
	RSC	14.35	15.67	16.92	17.81	12.48	13.11	13.74	16.54	18.90	17.72
	NO ₃ -N and NH ₄ -N	16.32	18.59	21.04	23.78	13.59	15.12	16.65	18.76	23.42	21.09

Effect of adsorbent dose on percentage reduction

A significant effect of changes in adsorbent dosage was observed on the removal percentages of BOD, COD, NO₃-N, NH₄-N, and RSC, with a p-value less than 0.05. The results indicate that, across all types of adsorbents, the dosage of 2.0 g exhibited the highest reduction percentage, initially showing an increase in

reduction percentage with rising dosage, followed by stabilization in the reduction process. This phenomenon can be attributed to the enhanced adsorption facilitated by the greater surface area and increased availability of adsorption sites. Ultimately, this effect leads to nearly maximal percentage reduction of pollutants when using 2.0 g of adsorbents^{18, 19, 20}.

Percentage reduction in BOD

RHA exhibited a percentage reduction of BOD ranging from 60-75% due to its high amounts of silica and carbon (Table 3). The silica particles in RHA possess a large surface area, enabling them to attract and retain organic compounds responsible for BOD^{21, 22}. Furthermore, the carbon content in RHA facilitated the adsorption of organic pollutants, thereby contributing to the reduction in BOD²³. Similarly, Sugarcane Bagasse abundant in cellulose, hemicellulose, and lignin, resulted in a reduction of BOD in the range of 56-66%. These complex organic compounds in SB possess excellent adsorption capacity, effectively attracting and retaining organic pollutants in the wastewater²⁴ and leading to reduced BOD levels. Ferric oxide sand, a modified form of sand with a layer of iron oxide, displayed a reduction in BOD within the range of 63-73%. This modification enhances the adsorption properties of the sand material by providing additional active sites and increasing the available surface area for adsorption.

Percentage reduction in COD

The rice husk ash yielded significant reductions in COD levels, with a range of 55% to 65%. This highlights the effectiveness of rice husk ash in purifying wastewater and eliminating organic pollutants. Similarly, when considering the implementation of sugarcane bagasse in wastewater treatment, a notable reduction in COD levels within the range of 50% to 60% was achieved. Fe-S, which exhibited COD reduction rates ranging from 51% to 61%. It takes advantage of the catalytic properties of iron, allowing for the efficient breakdown of organic pollutants and resulting in significant improvements in wastewater purity²⁶.

Percentage reduction in RSC

RHA and Fe-S demonstrated remarkable reductions in RSC, surpassing 100%. This exceptional result stems from the fact that, after treatment with RHA and Fe-S, calcium and magnesium concentrations increased, while carbonate and bicarbonate percentages decreased. Calcium and magnesium effectively displaced sodium ions, yielding a negative RSC value²⁶, leading to reductions exceeding 100%. Furthermore, RHA and Fe-S released calcium and magnesium ions into the water, enabling ion exchange with sodium ions, further increasing calcium and magnesium levels. These changes collectively contribute to a negative RSC

value. In contrast, sugarcane bagasse and charcoal achieved RSC reductions in the range of 50-60% when compared to RHA and Fe-S, indicating their relatively lower efficacy at a 2.0 g adsorbent dosage.

Percentage reduction in NO₃-N and NH₄-N

The reduction of NO₃-N and NH₄-N in wastewater, it was observed that the percentage reductions were not as high as some other parameters but still remained significant. RHA exhibited a reduction in the range of 35% to 55% for both NO₃-N and NH₄-N. SB demonstrated a reduction in the range of 35% to 45% for NO₃-N and NH₄-N. While the reduction percentages for SB were comparable to those of RHA, it is noteworthy that SB exhibited consistent performance across both nitrate and nitrite reductions. Iron coated sand demonstrated a reduction in the range of 34% to 45% for NO₃-N and NH₄-N.

Effect of contact time on percentage reduction of quality parameters

The impact of contact time on the removal percentage of BOD, COD, RSC, NO₃-N, and NH₄-N was examined using 2.0 g of adsorbent material and a wastewater load of 350 mL. Three contact durations of 5 min, 10 min, and 15 min were explored. Variations in contact time significantly influenced the percentage reduction of contaminants at a 5% level of significance, with a p-value of less than 0.05. The findings revealed a gradual increase in the percentage of reduction as contact time lengthened, reaching its maximum reduction at 15 min, after which it stabilized. For BOD, the use of RHA resulted in a noteworthy reduction, ranging from 50% to 70%. Similarly, both SB and Fe-S, achieved reductions in BOD within the range of 45% to 55%. In the case of COD, RHA demonstrated an effective reduction percentage ranging from 50% to 60%, while SB and SA exhibited COD reductions within the range of 45% to 55%. Remarkably, RHA showcased a reduction in RSC exceeding 100%, with Fe-S also achieving nearly 100% reduction of RSC. The materials RHA, SB, and Fe-S yielded percentage reductions in NO₃-N and NH₄-N ranging from 35% to 45%.

This can be attributed to the fact that as the contact time increases, contaminants have more time to interact with the adsorbents, leading to more effective adsorption. Initially, the sorption rate rises with longer contact times due to the greater availability of vacant sites on the adsorbent, facilitating more efficient removal in the early stages of contact. Nevertheless,

as contact time further extends, the rate of contaminant removal gradually decreases^{18,19}.

Effect of wastewater load amount on percentage reduction of quality parameters

The study explored the influence of wastewater quantity, specifically the wastewater load, while maintaining an optimized adsorbent dose of 2.0 g and a 15 min contact time. Three sample sizes, 200 mL, 250 mL, and 350 mL, were examined. The findings revealed an initial increase in percentage reduction from 200 mL to 250 mL, reaching a peak, but subsequently declining as the sample volume increased to 500 mL. The variations in sample load had a significant effect on the reduction of contaminants, as indicated by a p-value of less than 0.05. Regarding BOD reductions; RHA achieved a notable percentage reduction ranging from 60% to 75%, while treatment with Fe-S and SB yielded reductions in the range of 65% to 70%. For COD, RHA exhibited a percentage reduction ranging from 55% to 60%, SB showed similar performance, and Fe-S resulted in a reduction percentage of 50% to 55%. Remarkably, RHA displayed outstanding performance with a percentage reduction in RSC exceeding 100%, which was also observed with SB and Fe-S. However, the percentage reduction of NO₃-N and NH₄-N using RHA, SB, and Fe-S remained below 50%, falling in the range of 15-30% for these materials.

Thus, the optimal sample quantity for achieving the maximum percentage reduction of various parameters was found to be 250 mL of wastewater load. The observed trend of an initial increase in percentage reduction of contaminants with an increase in

wastewater load, followed by a decrease at higher loads, can be attributed to the adsorption dynamics within the system. The initial increase in percentage reduction of contaminants with rising wastewater load is likely due to the surplus of available adsorption sites relative to contaminant levels at lower volumes. However, as the load increases further, the available adsorption sites become limited compared to contaminant quantities, causing reduced effectiveness^{20, 24, 27}.

Adsorption kinetics and Isotherm study

Pseudo-first and pseudo-second-order models for adsorption

The study explored adsorption kinetics for BOD, COD, and RSC, employing pseudo-first and pseudo-second-order models, with results summarized in Table 4 and visualized in Fig. 7. In light of NO₃-N and NH₄-N reductions below 50% using the tested materials, conducting kinetic and isotherm studies for these contaminants was deemed unnecessary. Upon analysis it was observed that the pseudo first-order model did not provide a satisfactory fit for the adsorption of BOD, COD and RSC when plotting ln (q_e - q) against time (t). The correlation coefficient values for the pseudo first-order model were lower compared to those obtained for the pseudo second-order model. Similar findings have been reported by other researchers studying different adsorbent materials for the uptake of contaminants^{28,29,30}. Pseudo second order model assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. A linear relationship was obtained by plotting t/q_t against time (t), as shown in Fig. 7. By analyzing the t/q_t versus t

Table 4 — Kinetic model (first and second order) parameters for RHA, Fe-S and SB for the uptake of BOD, COD and RSC

Parameters	Pseudo-first order parameters			Pseudo-second order parameters			
	k ₁ (min ⁻¹)	q _e (mg/g)	R ²	k ₂ (g/mg/min)	q _e	R ²	
RHA	BOD	-0.00196	3.313	0.82	0.0440	11.189	0.99
	COD	-0.00097	1.416	0.81	0.1200	9.969	0.98
	RSC	-0.00036	0.881	0.77	0.373	2.916	0.99
Parameters	Pseudo-first order parameters			Pseudo-second order parameters			
	k ₁ (min ⁻¹)	q _e (mg/g)	R ²	k ₂ (g/mg/min)	q _e	R ²	
Fe-S	BOD	-0.00095	2.671	0.79	0.0591	9.436	0.99
	COD	-0.00141	2.535	0.85	0.0568	7.769	0.99
	RSC	-0.00199	0.287	0.91	0.3348	0.494	0.97
Parameters	Pseudo-first order parameters			Pseudo-second order parameters			
	k ₁ (min ⁻¹)	q _e (mg/g)	R ²	k ₂ (g/mg/min)	q _e	R ²	
SB	BOD	-0.00192	1.726	0.91	0.0926	7.948	0.99
	COD	-0.00150	3.408	0.88	0.0400	9.176	0.99
	RSC	-0.00103	0.432	0.85	7.394	0.175	0.99

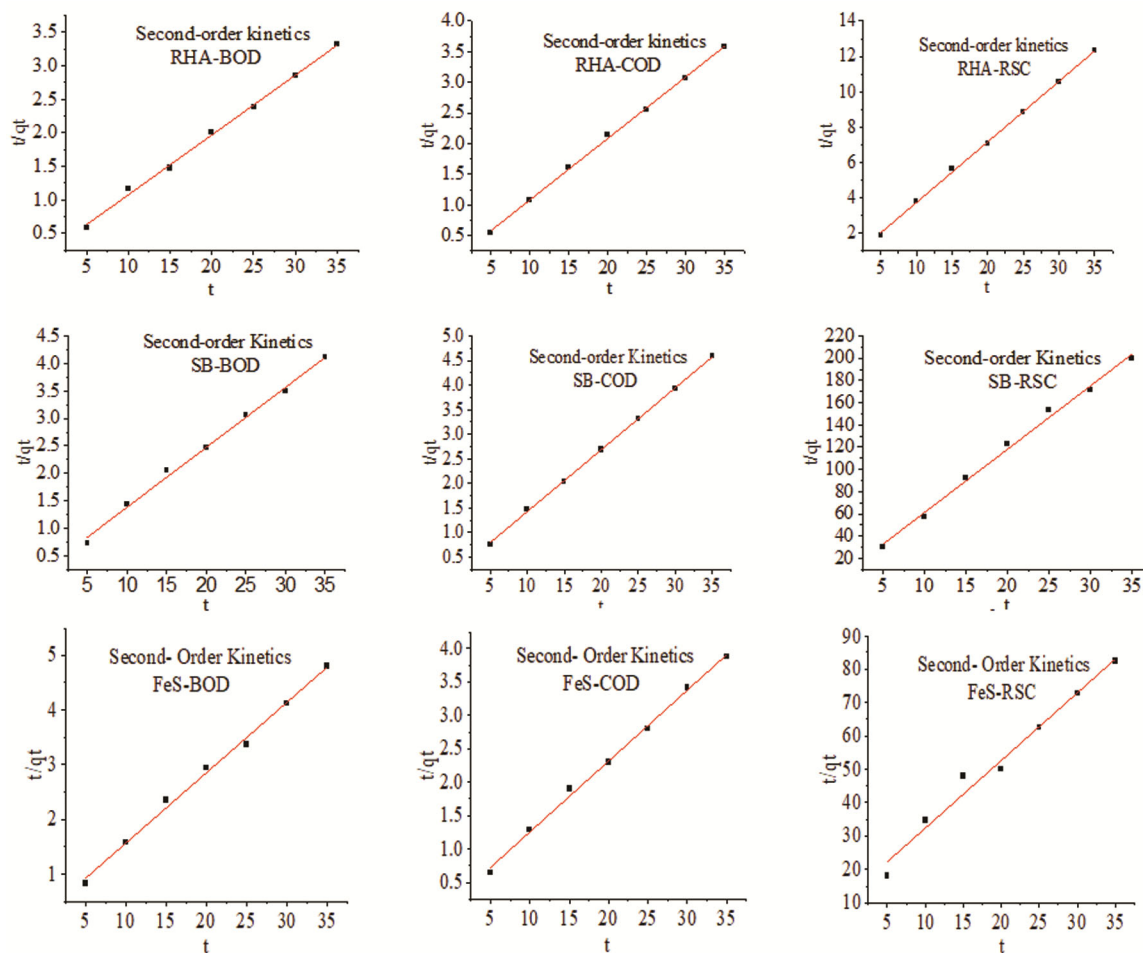


Fig. 7 — Pseudo second-order kinetic model for RHA, SB and Fe-S for the uptake of BOD, COD and RSC

plots, the values of k_2 (rate constant) and q_e (equilibrium adsorption capacity) were calculated and listed in Table 4. Based on the correlation coefficient values and the best fit of the experimental data, it can be concluded that the chemisorption reaction, which is characterized by the pseudo second-order kinetics, is the main adsorption mechanism for the removal of COD, BOD, and RSC from wastewater using RHA, Fe-S, and SB as adsorbents.

Langmuir and Freundlich isotherm models for adsorption

In the investigation of adsorption isotherms, plot was generated for the Freundlich isotherm by plotting $\text{Log}(C_e/q_e)$ against C_e , and for Langmuir isotherm by plotting $1/C_e$ against $1/q_e$. Both isotherm yielded straight lines with high correlation coefficients ($R^2 > 0.99$) observed in Freundlich isotherm (Fig. 8) indicating that the Freundlich isotherm model is applicable for the adsorption of COD and BOD from wastewater by RHA, Fe-S, and SB.

Similar findings have been reported by other researchers studying different adsorbent materials for the uptake of contaminants^{4, 29, 20, 31}. Because of the higher values of R^2 obtained in the Freundlich isotherm model compared to the Langmuir model, Freundlich isotherm model was chosen to describe the relationship between the adsorption capacities (q_e) of adsorbent materials (RHA, Fe-S, SB) and the residual amounts (C_e) of COD and BOD at equilibrium. The value of k_f was quite higher in comparison to q_{max} in Freundlich model. This suggests that the adsorption process follows favorable multilayer adsorption, indicating the presence of multiple layers of adsorbate molecules on the adsorbent surface. The Freundlich isotherm model assumes that there are no restrictions on the energy of adsorption sites and that adsorption can occur at various levels. This further supports the notion of multilayer adsorption, indicating that the adsorbent material can accommodate a significant amount of the adsorbate.

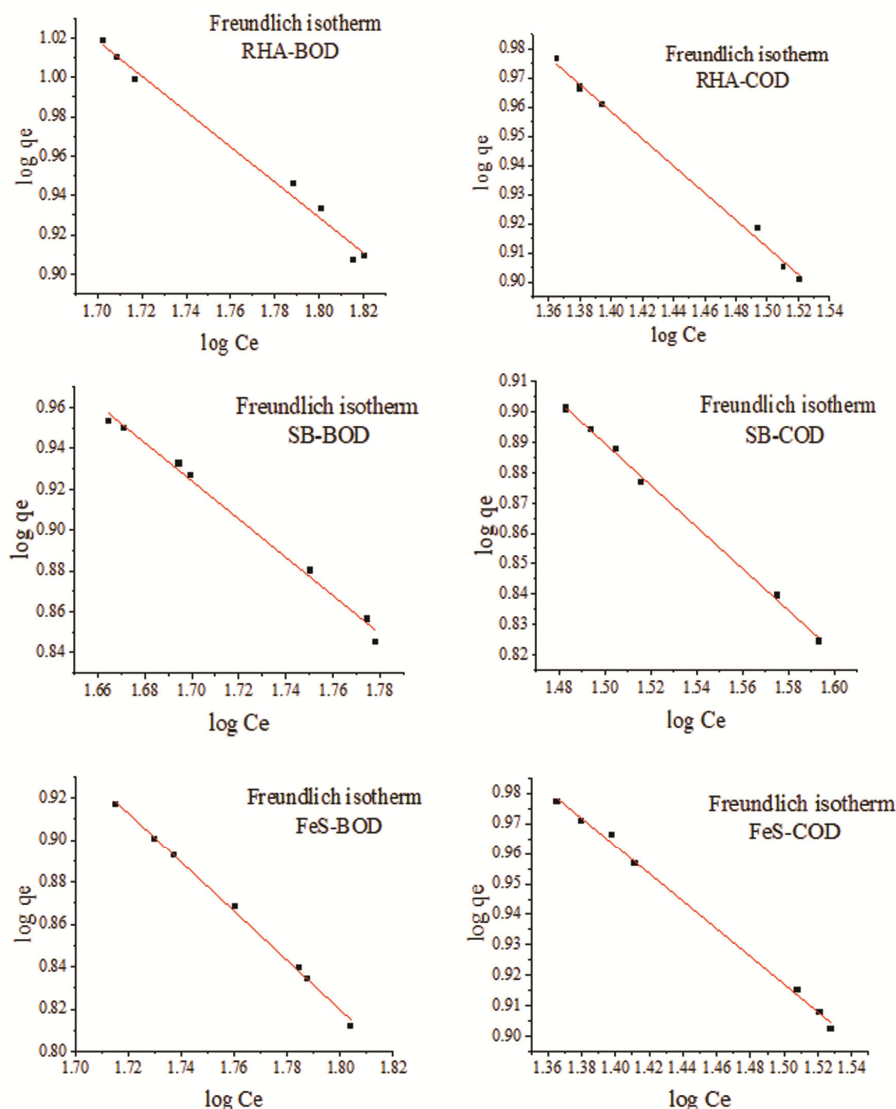


Fig. 8 — Freundlich model for RHA, SB and Fe-S for the uptake of BOD and COD

Conclusion

This study explored agricultural waste-based adsorbents for sewage water treatment, targeting irrigation quality standards. Initial assessments revealed high levels of pollutants - BOD, COD, RSC, $\text{NO}_3\text{-N}$, and $\text{NH}_4\text{-N}$. Rice husk ash, sugarcane bagasse, and ferric oxide sand (Fe-S) emerged as promising adsorbents, achieving significant pollutant reductions. Optimal conditions were identified: a 2.0 g adsorbent dose, a 15min contact time, and a 250 mL wastewater load were effective. Kinetic studies supported the pseudo-second-order model, indicating chemisorption as the primary removal mechanism for BOD, COD, and RSC with a strong correlation ($R^2 > 0.99$). Isotherm analysis

favoured the Freundlich model ($R^2 > 0.99$) for COD and BOD adsorption by RHA, SB, and Fe-S. This study identifies two agricultural waste materials, RHA and SB, as effective adsorbents for sewage water pollutant reduction, making it suitable for irrigation. Future prospects include developing filtration systems using these materials, possibly in combination with Fe-S. These eco-friendly solutions hold great promise for sustainable wastewater treatment, supporting environmental and agricultural sustainability. Examination of the post-treatment fate of adsorbents like rice husk ash, sugarcane bagasse, and ferric oxide-coated sand is vital for sustainable practices. After use, these materials can be responsibly disposed of or regenerated

for reuse. Future research can be focused on optimizing regeneration methods and exploring their integration into wastewater treatment plants, promoting resource recovery and minimizing environmental impact.

Acknowledgement

The authors are thankful to the Department Renewable Energy Engineering, Punjab Agricultural University for providing support in completion of lab work successfully

References

- Sato T, Qadir M, Yamamotoe S, Endoe T & Zahoor A, Global, regional and country level need for data on wastewater generation treatment and use Toshio, *Agric Water Mange*, 130 (2013) 1.
- Jha A, Chowdhury M & Satpute A N, Surface water quality forecasting using machine learning approach in *surface and groundwater resources development and management in semi-arid region*, Springer, (2023) 293.
- CPCB, Wastewater management for efficacious use of water resources, (2021) On line at: <https://pib.gov.in/PressReleaseDetail.aspx?PRID=1882807>.
- El-Nadi M H & Abd-Alla M A F, Removing heavy metals from wastewater by using rice husk wastes fiber, *Int Eng Adv Technol*, 8 (2019) 2249.
- Tzanakakis V A, Paranychianakis N V & Angelakis A N, Water supply and water scarcity, *Water*, 12 (2020) 2347.
- Raouf M E A, Maysour N E, Farag R K & Abdul-Raheim A M, Wastewater treatment methodologies, *Int J Environ Agric Sci*, 3 (2019) 018.
- Shokoohi R, Gillani R A, Mahmoudi M M & Dargahi A, Investigation of the efficiency of heterogeneous fenton-like process using modified magnetic nanoparticles with sodium alginate in removing bisphenol a from aquatic environments: Kinetic studies, *Desalin Water Treat*, 101 (2018) 185.
- Sarker N & Fakhruddin A N M, Removal of phenol from aqueous solution using rice straw as adsorbent, *Appl Water Sci*, 7 (2015) 1459.
- Wang J & Zhuang S, Removal of various pollutants from water and wastewater by modified chitosan adsorbents, *Environ Sci Technol*, 47 (2018) 2331.
- Qasem N A, Mohammed R H & Lawal D U, Removal of heavy metal ions from wastewater: A comprehensive and critical review, *NPJ Clean Water*, 4 (2021) 36.
- Kulkarni S J & Goswami A K, Adsorption studies for organic matter removal from wastewater by using bagasse flyash in batch and column operations, *Int J Sci Res*, 2 (2013) 180.
- Mahmoud M S & Mahmoud A S, Wastewater treatment using nano bimetallic iron/copper, adsorption isotherm, kinetic studies, and artificial intelligence neural networks, *Emerg Mater*, 4 (2021) 1455.
- Akl A A M, Dawy M B & Serage A A, Efficient removal of phenol from water samples using sugarcane bagasse based activated carbon, *J Anal Bioanal Technol*, 5 (2014) 1.
- Singh B & Thakur V, Eco-friendly and cost-effective use of rice straw in the form of fixed bed column to remove water pollutants, *J Bioremed Biodegrad*, 7 (2016) 1.
- Mushtaq F, Zahid M, Bhatti I M, Nasir S & Hussain T, Possible applications of coal fly ash in wastewater treatment, *J Environ Manage*, 240 (2019) 27.
- Begum R & Desai J P, Treatment of industrial wastewater by using sugarcane bagasse, *Int Res J Eng Tech*, 6 (2019) 1.
- Bello O S, Bello I A & Adegoke K A, Adsorption of dyes using different types of sand: A review, *S Afr J Chem*, 66 (2013) 117.
- Gulipalli C S, Prasad B & Wasewar K L, Batch study, equilibrium and kinetics of adsorption of selenium using rice husk ash (RHA), *J Eng Sci Technol*, 6 (2011) 586.
- Mandal A & Das S K, Phenol adsorption from wastewater using clarified sludge from basic oxygen furnace, *J Environ Chem Eng*, 7 (2019) 103259.
- Priya A K, Yogeshwaran V, Rajendran S, Hoang T K, Soto-Moscoco M, Ghfar A A & Bathula C, Investigation of mechanism of heavy metals (Cr^{6+} , Pb^{2+} & Zn^{2+}) adsorption from aqueous medium using rice husk ash: Kinetic and thermodynamic approach, *Chemosphere*, 286 (2022) 131796.
- Ahmaruzzaman M, A review on the utilization of fly ash, *Progress Energy Comb Sci*, 36 (2010) 327.
- Seaf-El-Nasr T A, Gomaa H, Emran M Y, Motawea M M & Ismail A R A, Recycling of nanosilica from agricultural, electronic, and industrial wastes for wastewater treatment in *Waste Recycling Technologies for Nanomaterial Manufacturing*, Springer, (2021) 325.
- Singh V, Kaur A & Gupta N C, Comparative analysis of the filtration potential of light greywater through various media, *Malays J Sci*, (2020) 159.
- Yogeshwaran V & Priya A K, Experimental studies on the removal of heavy metal ion concentration using sugarcane bagasse in batch adsorption process, *Desalin Water Treat*, 224 (2021) 27160.
- Khan J, Lin S, Nizeyimana J C, Wu Y, Wang Q & Liu X, Removal of copper ions from wastewater via adsorption on modified hematite ($\alpha\text{-Fe}_2\text{O}_3$) iron oxide coated sand, *J Clean Prod*, 319 (2021) 128687.
- Kumar P S & Balamurugan P, Evaluation of groundwater quality for irrigation purpose in attur taluk, Salem, Tamilnadu, India, *Water Energy Int*, 61 (2018) 59.
- Patel H, Environmental valorisation of bagasse fly ash: A review, *RSC Adv*, 10 (2020) 31611.
- Sharma P, Kaur R, Baskar C & Chung W J, Removal of methylene blue from aqueous waste using rice husk and rice husk ash, *Desalination*, 259 (2010) 249.
- Hanumanthappa S, Guruswamy A D, Eshanna M S & Gaonkar G V, Removal of cod from real textile wastewater using three low-cost adsorbents-its kinetic models and adsorption isotherms, *Int J Environ Anal Chem*, (2022) 1.
- Dutta S, Srivastava S K & Gupta A K, Polypyrrole-polyaniline copolymer coated green rice husk ash as an effective adsorbent for the removal of hexavalent chromium from contaminated water, *Mater Adv*, 2 (2021) 2431.
- Yang Y, Nguyen T M P, Van H T, Nguyen Q T, Nguyen T H, Nguyen T B L & Yilmaz M, ZnO nanoparticles loaded rice husk biochar as an effective adsorbent for removing reactive red 24 from aqueous solution, *Mater Sci Semiconduct Process*, 150 (2020) 106960.