Original Research Article

Quality Minimization of Agricultural Drainage Water for Irrigation Water Reuse Using Coconut Shell Activated Carbon

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ABSTRACT

Nutrients and organic pollutants draining from agricultural fields are the leading sources of surface water quality impairment. Activated carbon (AC) produced from agricultural crop residues has great success in the sequestration of hazardous substances from wastewaters. This study evaluates the potential of coconut shell activated carbon for agricultural drainage water quality minimization; pH adjustment, and excess nitrate and sulphate adsorption. Agriculture drainage water samples were collected and analyzed for Electrical conductivity, Total Dissolved Solids, Chloride, Sodium, Sulphate, Bicarbonate, Nitrate – Nitrogen, and pH. Coconut shells were sourced locally and carbonized at 500 °C (± 5^{o}C) for one hour in a muffle furnace. The char produced was ground, sieved, and activated with Phosphoric acid (KOH). The porosity and morphological structures of the AC were examined using a Scanning Electron Microscope. The effect of contact time (30, 60, 90, and 120 min), temperature (20 and 40 °C), and adsorbent dosage (1, 1.5, 2, and 2.5 g) were examined using batch studies. The analysis of the drainage water shows the water is highly alkaline and contains sulphate and nitrate above FAO benchmark values. The SEM analysis indicates that the stability and mesoporosity of the carbonaceous material were enhanced by KOH activation. The pH value of the treated water decreased from 9.94 (highly alkaline) to 7.92. The use of 1 g (10 g/l) of coconut shell AC has the highest amount of nitrate and sulphate per unit quantity of AC (4.1 and 2.98 mg/g respectively). The adsorption process peaked at 30 mins contact time with 99.8% and 98.8% nitrate and sulphate removal efficiency, respectively. The process is temperature dependent; nitrate adsorption performs slightly better at 40 °C; sulphate adsorption at 20 °C. More research effort is needed to ascertain the performance and applicability under continuous flow conditions.

Keywords: Activated carbon; Agricultural Drainage Water; Coconut Shell; Irrigation

1. INTRODUCTION

In recent decades, agricultural growth has translated into gains in economic and human development; improvements in food security, increase export and reductions in household poverty [1], [2]. Howbeit increased agricultural production is no longer sustainable without compromising ecological integrity and environmental quality [3]. Nutrients and organic pollutants from agriculture are the leading sources of surface water quality impairment via unrestricted use of fertilizer and pesticides and indiscriminate dumping of animal waste, plant residue and Agro-industry by-products in the open environment [4], [5]. Also, irrigated agriculture which accounts for more than 45% of total agricultural production is under fierce competition with other sectors for freshwater [6]. The misuse and overuse of water resources and fertilizers for agriculture are no longer sustainable, and the productivity of these resources needs to increase [7]. Agricultural drainage reuse facilitates efficient water and nutrient management and keeps pollutants out of the water, soil, and food sources downstream [8].

Excess irrigation water is the largest subset of agricultural wastewater; reuse of this water could be a valuable source in the face of the growing demand for freshwater for agriculture [9]. Water not consumed by crops is a critical component of water resources for subsequent irrigation via reuse strategies, such as blending and cycling [8]. This water is commonly used for irrigation by downstream agricultural producers but can also potentially be reused in the same region as supplemental irrigation water. This practice will ensure sustainable use of groundwater for food production and reduce the cost of pumping and energy requirement for irrigation [3]. Quality minimization of and reuse of agricultural drainage water are not limited to providing irrigation water, but it is also essential to prevent freshwater salinization, eutrophication, and other environmental pollution [10].

Like other nontraditional water sources, the reuse of agricultural drainage poses new challenges as irrigation water [10]. Drainage water quality reflects the source water quality, soil water constituents and agricultural chemicals applied to the soil being drained [11]. Drainage water emanating from some regions are a nutrient source (N and P), making direct reuse on-site with minimal treatment feasible and enhancing a closed and environmentally favourable nutrient cycle [12]. In other regions, drainage water contains critical constituents affecting plant and soil conditions during long-term application, preventing reuse without treatment [13]. The presence of heavy metals had been reported in regions where Agricultural drainage water mixed with municipal or industrial wastewater [9], [14]. Such water can pose serious health hazards as nitrates and heavy metals bioaccumulate in plants [15], [16]. Drainage water can also contain high levels of salts, excess soluble salts in irrigation water will concentrate in the root zone and limits the capacity of plants to absorb water and nutrients [17]. Agricultural drainage can potentially include other constituents such as pesticides, microbes or CECs. Hence the need for low-cost wastewater treatment systems that fulfil the objective of agricultural reuse.

Several remediation processes such as oxidation, filtration, ion exchange, biological treatment, flocculation, sedimentation and coagulation have been recommended for the treatment of Agricultural drainage water [13]. However, adsorption techniques have been acknowledged as the most economical and highly efficient method. [18], [19]. Conventional treatment techniques suffer drawbacks due to high operational and maintenance costs, high energy requirements, sludge formation and disposal, nonbiodegradable side products, and complicated management [20], [21]. Contrarily, adsorption is highly efficient for removing a wide range of pollutants, requires less operation cost and is simple to operate and manage [22]. However, commercial available AC is expensive and requires regeneration [23]. Hence, the advocates for low-cost adsorbents from agricultural wastes, industrial solid wastes, and biomass [24], [25].

Agricultural crop residues (ACRs), as lignocellulosic materials, have a huge potential to be used as carbon precursors for AC [20], [21]. Agriculture generates a huge amount of crop residues such as corn cobs, rice husks, wheat straw, groundnut husks, and coconut shells which are rich in carbon, have high volatile matter content, low inorganic content and degrade slowly in storage [18], [26]. In developing economies, most of this residue is misled or discarded as waste due to a lack of focus on reuse for more economic and environmental benefits [27], [28]. They are either underutilized or disposed of by burning, dumping or unplanned landfilling which results in methane emissions and other environmental hazards [29], [30]. Among the possible alternative uses of crop residues, the production of activated carbon seems to strengthen the comprehensive utilization for sustainable agriculture.

Activated carbon produced from ACRs has been proven to be sustainable, environmentally friendly, economical, and efficient in liquid-phase adsorption applications; industrial and wastewater treatment [18], [21], [31], heavy metals adsorption [32], [33], water purification [31], [34]. AC from ABPs have great success in the sequestration of hazardous substances from the environment; benzene [35], phenol [23], [36], dyes, and crude oil components[22]. Recent studies tend to advocate the modification of ACRs to improve their adsorption capacity. Carbonization of ACRs results in char with disorganized carbon, minimal surface area and tar-filled pores. Activation via thermal and chemical methods enlarges the pore diameter, extends the surface area, enhances the yield and creates new micro-structures in the char [37]. Thermal activation is achieved via carbonization in an inert atmosphere and gasification in the presence of an oxidizing gaseous (steam, air, CO2 or mixture) at high temperatures [38]. In chemical activation, the lignocellulosic precursor is impregnated in a chemical activator (H_3PO_4, H_2SO_4, $ZnCl_2$, HNO_3 and NaOH) and carbonized at intermediate temperature [39].

In this study, coconut husks, an agricultural residue, were used to produce highly porous AC via thermal and chemical activation methods. The objective of this work is to evaluate the potential of coconut shell AC for agricultural drainage water quality minimization; pH adjustment, and excess nitrate and sulphate adsorption.

2. MATERIAL AND METHODS

2.1 Water Sample Collection

Assessment of drainage water quality is necessary when treating the water for disposal or reusing the water for irrigation. Water samples were collected from drainage at Oke – Oyi irrigation project site of the Lower Niger River Basin Development Authority in the western part of Nigeria; latitude 8° 24 N and 83° 6 N and longitude 4° 10 E 4° 36 E. The samples were collected in triplicate from the main drains (Fig. 1). The samples were collected in 12L sampling bottles that have been previously washed with nitric acid, and thereafter rinsed with distilled water to disinfect the bottles. The collected samples were filtered using 0.45 µm Whatman® filter paper. After collection, the sample bottles were sealed, marked, and placed in an ice pack container and thereafter transferred to the laboratory for further analyses. In the laboratory, the samples were kept in the refrigerator at 4 °C, and all analyses were done within 48 h. The drainage water was analyzed for Electrical conductivity, Total Dissolved Solids, Chloride, Sodium, Sulphate, Bicarbonate, Nitrate – Nitrogen and Acid/Basicity.

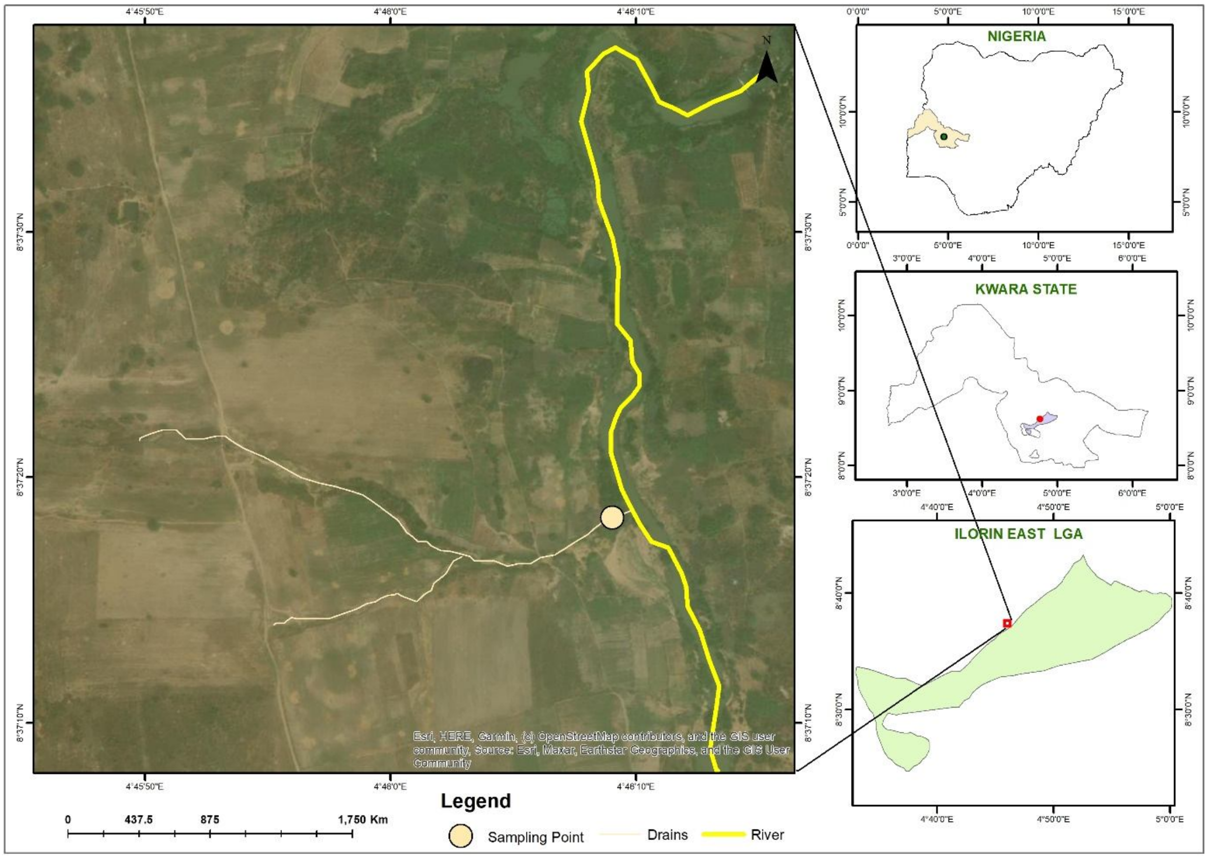

Fig. 1. Drainage water sampling point

2.2 Coconut Shell Charcoal

The carbonaceous precursor, coconut shells, were collected from *"Arada Market"* within the Ogbomoso metropolis (8° 8´ 31.79" N, 4° 1´ 42.67" E), Oyo State, Nigeria. The samples were washed with distilled water and dried in an oven at 120^{o}C for 1½ hours. The shell was carbonized at 500 ˚C (± 5^{o}C) for one hour using an electric muffle furnace (flow rate 100 ml/minute) which allows for limited air supply. The char produced was cooled in a desiccator, and then crushed with a jaw laboratory crusher (48-D0530/A). The sample was grinded and sieved with a Gilson Tapping 8-inch sieve shaker (230V/50Hz)). The activated carbon was sieved using sieves of different sizes (2mm, 1mm, 850µm, 710µm, 500µm, 425µm, 300µm, 250µm,150µm, 63µm, and pan) arranged in descending order on an electric vibrator, to vibrate the sample for a period of 5minute. Thereafter, the sieve fractions were collected and weighed respectively.

2.3 Chemical Impregnation

The char produced was activated by using phosphoric acid (KOH) in the ratio of 1 gram of carbonized coconut shell to 8 mL of 0.3M phosphoric acid (KOH) for 24 hours. The sample was dried at 100±5^{0}C for 3 h. After activation, excesses of KOH were washed with hydrochloric acid (1M HCl) and deionized water until pH 7 was obtained. The sample was then oven dried at 110˚C for 12 h and kept in an air-tight container.

2.4 AC Morphology

The porosity and morphological structures of the activated carbon samples were investigated before and after activation using a Scanning Electron Microscope (ASPEX 3020 PSEM 2) operated at 16kV.

2.5 Adsorption Experiments—Batch Studies

The studies were performed for assessing the adsorption efficiency of sulphate and nitrate from irrigation drainage water using coconut shell AC. Process variables such as contact time (30, 60,80 and 120 min), temperature (20 and 40 ▪ C) and adsorbent dosage (1, 1.5, 2 and 2.5 g) were varied during the experiment. Irrigation drainage water (100 mL) was missed with specific dosages of the AC in a 250 mL stopper conical flasks. The solution was agitated from 30 to 180 min in a water bath shaker. At the end of the specific contact time, the residue was filtered out while the pH, nitrate and sulphate concentration was determined in the filtrate using a spectrophotometer (Model No: U V752 (D)). The experiments were repeated in triplicate and the average was used for accuracy and to check reproducibility. The percentage of nitrate and sulphate removal is derived from

$$\% \text{ removal} = \frac{C_o - C_t}{C_o} \times 100\%$$

where C_o and C_t are nitrates or sulphate concentrations initially and at a specific time (mg/L), respectively. The adsorption capacity (qt), the amount of nitrate and sulphate adsorbed per unit quantity of coconut shell AC, was calculated using Equation (2):

$$q_t = \frac{C_o - C_t}{m_s}$$

where m_s is the amount of coconut shell AC added in gram.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of Water

The chemical characteristics of the drainage water used are presented in Table 1. The water is highly alkaline, and has excess sulphate and nitrate concentration with relative high sodium content compared with FAO guideline values. The pH of the drainage water is highly alkaline (9.4) and out of range of the FAO benchmark value for suitable irrigation water. Irrigating with such water increases the root-zone pH and inhibits plant access to nutrients; Mg, Ca, P, Fe, Mn, Zn [40]. In addition, irrigation water with high pH can clog injectors and drip lines with deposits of calcium and magnesium phosphates and carbonates [41]. Sulphate is a major ion present in natural waters; its enrichment in the sampled water could have originated from chemical weathering and dissolution of highly soluble sulfate-bearing minerals found in Precambrian rocks [42]. Decaying organic matter, sewage, fertilizers and manures are the main sources of nitrates in irrigation water. Nitrate in the irrigation water has the same effect as applying nitrogen fertilizer to the soil. Freshwater, surface and groundwater, usually have less than 5 mg/l nitrate concentration [42], [43]. Howbeit, high levels of nitrate are found in drainage water due to the deep leaching of fertilizers [44]. Crops differ in their tolerance to nitrate in irrigation water; some crops are sensitive above 5 mg/l, and others can tolerate up to 30 mg/l of Nitrate [45]. High concentrations of nitrate as found in the sampled water (41.5 mg/L) may over-stimulate growth, delay maturity or cause poorer quality yield in commonly grown crops [15]. The enrichment of the anion (SO_4^{2-} and NO_3-N) in the sampled water encourages the growth of algae and other aquatic plants that may produce undesirable tastes and odours in rivers, streams, and lakes [46].

Table 1. Constituents' Analysis of Drainage Water

S/N	Water Parameter	Symbol	Analytical Results	Permissible Range (FAO)
	Salinity			
1.	Electrical conductivity (ds/m)	ECw	0.036	0 – 3
2.	Total Dissolved Solids (mg/l)	TDS	33.90	0 – 2000
	Cations and Anions			
3.	Chloride (mg/l)	CL^-	1.19	0 - 1062.5
4.	Sodium (mg/l)	Na^+	748	0 - 919.6
5.	Sulphate (mg/l)	SO_4^-	30	0 – 20
6.	Bicarbonate (mg/l)	HCO_3^-	0.15	0 - 6102
	Nutrients			
7.	Nitrate – Nitrogen(mg/l)	NO_3^-N	41.5	0 –10
	Miscellaneous			
8.	Acid/Basicity	pH	9.94	6.50 – 8.40

3.2 Surface Morphologies of the Adsorbents

The scanning electron microscopic (SEM) analysis was carried out for structural and morphological characteristics of coconut shells before and after activation. The micrograph of the coconut shell before activation is presented in Figures 1a and 1b; the morphology is observed to be lumpy solid. The activated coconut shell, Figure 1c, shows a more irregular surface and circular dark spots which represent pore openings and cavities. The chemical and thermal activation enhanced the stability and mesoporosity of the carbonaceous material as depicted by the uniform distribution of the pores. These openings facilitate the solution to flow into the pore and enhance the adsorption kinetics [36]. However, the surface characteristics were slightly degraded, and several irregular shape large holes appeared on the surface at higher display magnification, Figures 1d and 1e. The degraded surface result from the conversion of more micropores to large mesopores and macropores as burning time increases. Pore sizes increased initially with burning time and then began to collapse with longer burning times [19].

Fig. 2. Surface morphology of the sample before Activation (a and b at 1000um) and after activation (c and e at 100 um, d and f 20um)

3.3 pH Adjustment using Coconut Shell AC

Good quality irrigation water has circumneutral pH. Irrigation water pH influences the soil pH and consequently the absorption of macro and micronutrients by the plant [41]. Therefore, when considering nontraditional water sources for agricultural purposes, it is essential to optimise the water pH for symbiotic effects between the soil and the plant [47]. The effects of adsorption on the water pH are presented in Figure 3. The pH value of the treated water is slightly alkaline compared to the highly alkaline drainage water. The final pH value falls within the permissible range of irrigation water as stated by FAO; 6.5-8.4. Water in this pH range: maintains nutrient balance and prevents scale formation in irrigation systems [41]. Traditionally, water pH is reduced by acidification. However, this method has several consequences that are eliminated by the use of AC; the cost and the downside of chemical input in agriculture, scaling and clogging of pipes and drippers and handling and storage of acids. As the popularity of AC as a water treatment alternative is increasing, AC can be a substantial tool for pH adjustment in alkaline water.

Fig. 3. Comparison of pH before and after treatment and the FAO standard

3.4 Effect of Processing Variable on Absorption

The activated carbon was evaluated for its nitrate and sulphate removal efficiency using agricultural drainage water. The following parameters were considered; adsorbent dosage, contact time and temperature.

3.5 Adsorbent Dosage Variation

The ability of coconut shell AC to remove nitrate and sulphate in agricultural drainage water at various dosages is shown in Fig. 4. Evaluation of the effect of different adsorbent dosages (1.0- 2.5 g) on the removal of nitrate revealed that the use of 1 g (10g/l) of coconut shell AC was able to remove the highest amount of nitrate and sulphate per unit quantity of coconut shell AC (4.1 and 2.98 mg/g respectively) at the shortest contact time of 30 min. An increase in the dosage caused the adsorption slopes to become gentle and absorbance per unit quantity to decrease exponentially. This implies that there are fewer nitrate and sulphate molecules than the available adsorption sites [48].

3.6 Contact Time Variation

The adsorption curve, Fig 4, shows that the retention time of the sulfate and nitrate ions is within 30 min of the contact time. The adsorption capacities reached their climax (4.1 and 2.98 mg/g for nitrate and sulphate, respectively) within this period and remain constant for the remaining time. A similar absorption time of 20 to 30 mins was reported for sulphate ions adsorption from aqueous solutions using modified wool fibres [48].

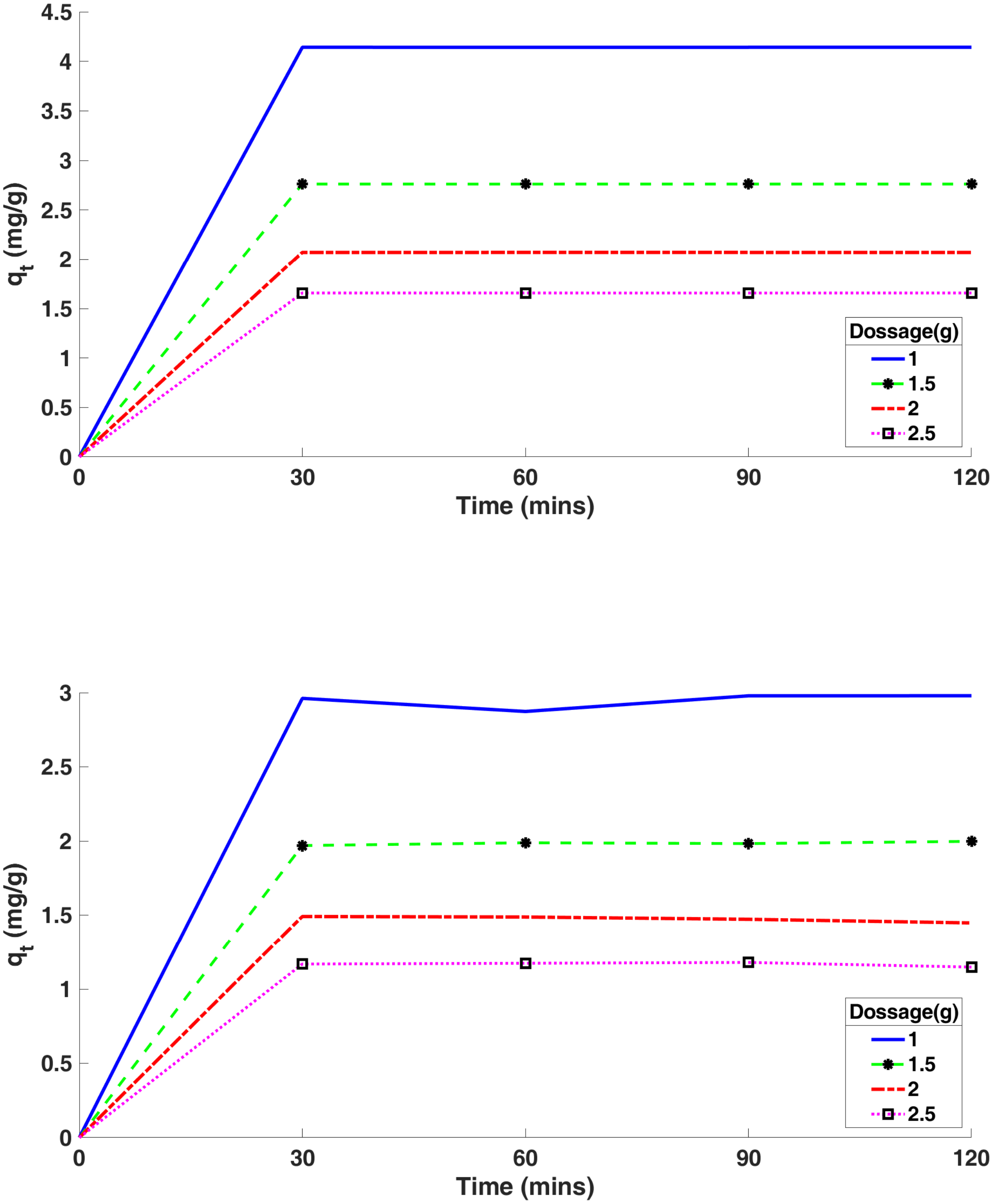

Fig. 4. Adsorption capacity at various dosages: a.) Nitrate, b.) Sulphate

3.7 Temperature Variation

The experiment was carried out at 20 and 40 °C at varying adsorbent doses, 1- 2.5 g. The plot of percentage removal of nitrate and sulphate versus temperature is presented in Fig. 5. The maximum adsorption percentage was 99.8% and 98.8% for nitrate and sulphate respectively. The removal efficiency of nitrate is slightly better at higher temperatures (40 °C), indicating the endothermic nature of adsorption [25]. As reported by [49], sulphate adsorption seems to perform better at a lower temperature (20 °C). This implies that the sulphate and nitrate adsorption process is a temperature-dependent process and the optimum adsorption temperature must be determined.

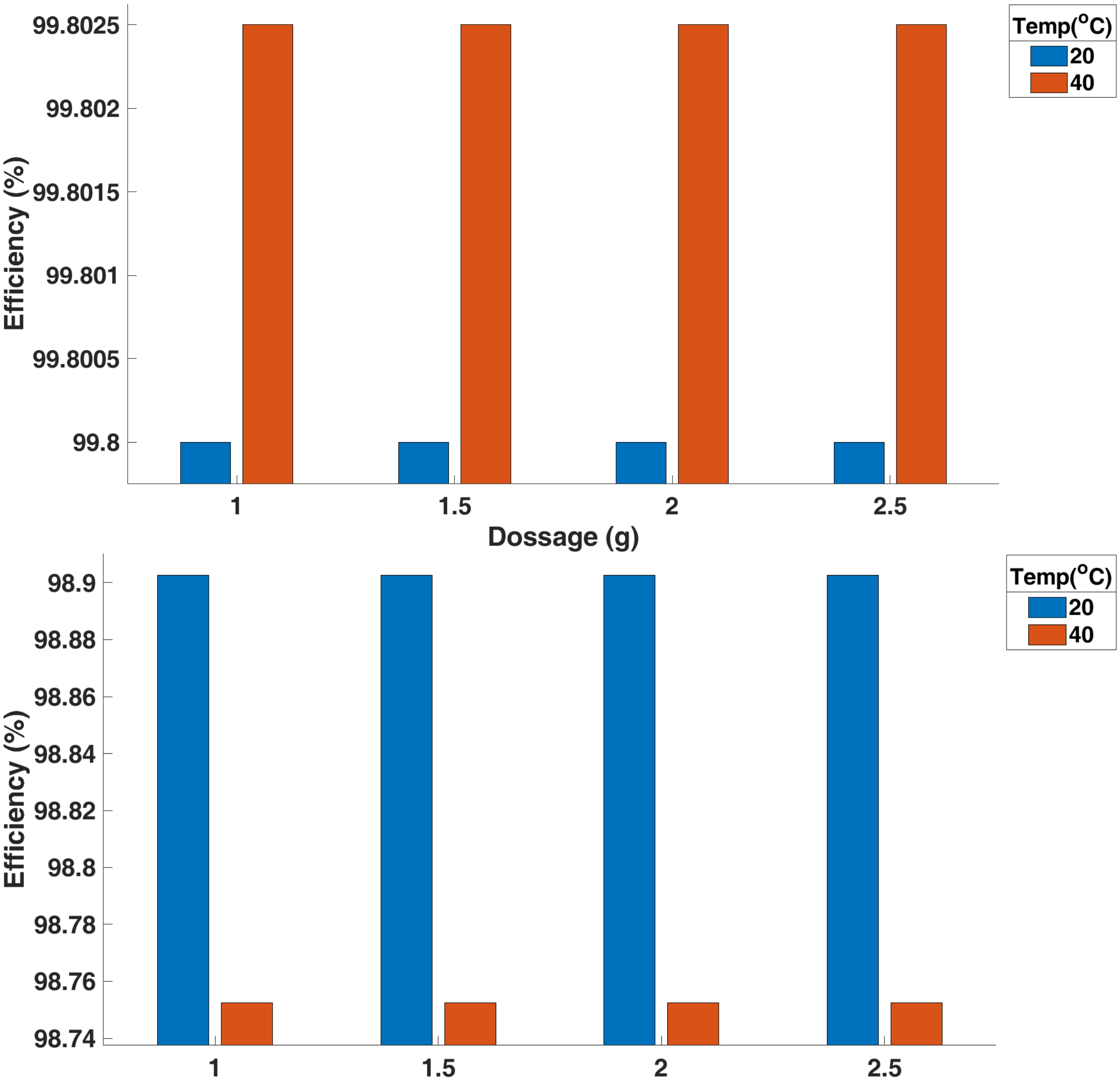

Fig. 5. Removal efficiency against Dosage: a.) Nitrate b.) Sulphate

4. CONCLUSION

Coconut-shell activated carbon showed the potential as a sustainable adsorbent alternative for pH adjustment and minimization of excess nitrate and sulphate in Agriculture drainage water. The SEM image showed that the pore sizes increased initially with burning time and then began to collapse with longer burning times. Adsorption of agriculture drainage water with AC derived from coconut shells effectively adjusts the drainage water pH from 9.94 (highly alkaline) to 7.92. The adsorption process reached equilibrium within 30 min at a maximum sorption rate of 4.1 and 2.98 mg/g for nitrate and sulphate, respectively. The maximum adsorption percentage was 99.8%. and 98.8% for nitrate and sulphate respectively. More research effort is needed to enhance the adsorption capacity and evaluate the performance and applicability under continuous flow conditions.

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