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Original Article

Phosphorus And Nitrogen Removal Performance Of Zeolite And Rice Husk From Wastewaters

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ABSTRACT

Nitrogen and phosphorus-rich wastewater effluents result in the eutrophication of water resources and threaten aquatic life. Therefore, aquatic life can be supported by wastewater treatment. In this study, filter column tests assessed the phosphorus and nitrogen removal performance of both zeolites, abundantly available in Türkiye, and rice husk, abundantly available waste material, from synthetic wastewaters. Materials were used alone and in mixtures (25:75, 50:50, and 75:25). Phosphorus and nitrogen solutions at different concentrations (0, 10, 25, and 50 mg L^{-1}) pass through filter media at a flow rate of 5.0 mL/min. Effluent samples taken at the end of the 3rd, 6th, 12th, 24th, and 48th hours were subjected to pH, electrical conductivity (EC), total phosphorus (TP), and total nitrogen (TN) analyses. The highest nitrogen removal efficiency (75.1%) was achieved with 75:25 zeolite: rice husk mixture at the end of the 3rd hour from 10 mg L^{-1} influent concentration and the lowest with the same mixture at the end of the 48th hour from 50 mg L^{-1} influent concentration. The highest phosphorus removal efficiency (19.4%) was achieved with pure zeolite at the end of the 3rd hour from 10 mg L^{-1} influent concentration and the lowest (0.14%) with 25:75 zeolite: rice husk mixture at the end of the 48th hour from 50 mg L^{-1} influent concentration. Based on the present findings, it was concluded that rice husk further improved the nitrogen removal efficiency of zeolite.

Keywords: Column studies, nitrogen, phosphorus, rice husk, zeolite

Atık Sulardan Zeolit Ve Pirinç Kabuğunun Fosfor ve Azot Giderim Performansının Belirlenmesi

ÖZ

Azot ve fosfor açısından zengin atıksu deşarjları, su kaynaklarında ötrofikasyona yol açarak sucul yaşamı tehdit etmektedir. Bu nedenle, atıksuların arıtılması ile sucul yaşam desteklenebilir. Bu çalışmada, Türkiye'de bolca bulunan zeolit ve atık malzeme olarak bolca bulunan pirinç kabuğunun, sentetik atıksulardan fosfor ve azot giderme performansı, filtre kolon testleriyle değerlendirilmiştir. Malzemeler hem tek başlarına hem de karışımlar halinde (25:75, 50:50 ve 75:25) kullanılmıştır. Farklı konsantrasyonlardaki fosfor ve azot çözeltileri (0, 10, 25 ve 50 mg L^{-1}) filtre ortamından 5.0 mL/dakika debiyle geçirilmiştir. 3. saat, 6. saat, 12. saat, 24. saat ve 48. saat sonunda alınan effluent örnekleri pH, elektriksel iletkenlik (EC), toplam fosfor (TP) ve toplam azot (TN) analizlerine tabi tutulmuştur. En yüksek azot giderme verimliliği (%75.1), 10 mg L^{-1} giriş konsantrasyonundan 3. saatin sonunda, 75:25 zeolit:pirinç kabuğu karışımıyla elde edilmiştir; en düşük verimlilik ise aynı karışımla 48. saatin sonunda 50 mg L^{-1} giriş konsantrasyonunda elde edilmiştir. En yüksek fosfor giderme verimliliği (%19.4), 10 mg L^{-1} giriş konsantrasyonundan 3. saatin sonunda saf zeolit ile elde edilmiştir; en düşük verimlilik ise (%0.14) 50 mg L^{-1} giriş konsantrasyonundan 48. saatin sonunda 25:75 zeolit:pirinç kabuğu karışımıyla elde edilmiştir. Elde edilen bulgulara dayanarak, pirinç kabuğunun zeolitin azot giderme verimliliğini artırdığı sonucuna varılmıştır.

Anahtar kelimeler: Azot, Fosfor, Kolon çalışmaları, Pirinç Kabuğu, Zeolit

INTRODUCTION

By 2015 and 2030, the world's population will grow to approximately 7.2 and 8.3 billion, respectively. Significant improvements in food production are necessary in such a situation. There are several ways to increase food production: farming more land, raising crop yields, planting two or three crops annually on the same plot of acreage, or combining these methods. They all have different benefits and drawbacks, however. Some other options call for more labor-intensive production techniques. For example, use mechanization, high-yield cultivars, irrigation, fertilizers, and pesticides (Özkay et al., 2014).

Water is an indispensable component of life on Earth. Although 75% of the world is covered with water, it does not necessarily mean water is abundant. Only 0.75% of water resources are drinkable. The world population, approximately 1 billion at the end of the 18th century when the Industrial Revolution began, has reached 7.92 billion. With a rapidly increasing population, domestic, industrial, and agricultural water needs have also increased. Besides these increasing needs, global warming and climate change seriously pressure available water resources. Developing industries and technology are insufficient for treating wastewater (Vo et al., 2014).

According to long-term research of the International Water Management Institute (IWMI), countries with an available water resource of <1700 m^3 per capita are classified as “water-stressed” countries. On the other hand, countries with an available water resource of < 1,000 m^3 are classified as “water-poor” countries (IWMI, 2023).

Türkiye has an annual total available water resources of 112 billion m^3 and a population of 85 million. Therefore, the annual amount of available water resources per capita is approximately 1315 m3 (112 billion / 85 million). With that value, Türkiye is classified among the water-stressed countries (DSI, 2022). Given the nation's limited water supplies, reusing low-quality or treated water is crucial for agricultural irrigation. However, pollutants such as heavy metals and trace elements found in treated waters can cause several issues for plants and soils (Özkay et al., 2014).

Therefore, reuse of water resources has become a prominent issue. Wastewater primarily contains nitrogen, phosphorus, pathogenic organisms, heavy metals, and trace organic pollutants. Nitrogen and phosphorus pollution mainly result in the eutrophication of water resources, thus adversely affecting water quality, and these waters cannot be used as drinking water. Such pollution threatens aquatic life (USEPA, 1988; Eugenia Valsami, 2004; EEA, 2006).

Nitrogen may generate dangerous ground water pollution and pose serious environmental and human health risks. Spalding and Exner (1993) indicated nitrate as groundwaters' most common chemical pollutant. Nitrate-contaminated waters can reach surface waters through groundwater flows, disrupt nitrogen-phosphorus balance, and result in algae formation and eutrophication of these environments (Bolger & Stevens, 1999). Agrochemicals constitute the most significant source of nitrate in groundwaters.

Intensive use of cleaning chemicals, such as detergents, soaps, and shampoos, generates phosphorus pollution of water. Various methods, such as activated carbon, reverse osmosis, and electrodialysis, are used for phosphorus removal from wastewater (Yeoman et al., 1988). Recent research primarily focused on phosphorus removal using adsorbent solid media.

Water resources that are already used are considered wastewater. Wastewaters have to pass through treatment processes not to alter the physical, chemical, and ecological characteristics of the environments into which they are discharged (SKKY, 2004). Various treatment methods are used to reuse water resources. These methods include physical processes (aeration, sieves, and filters), biological processes (anaerobic treatment and oxidation), chemical processes (neutralization, disinfection, and flocculation), and membrane processes (filtration and osmosis) (Rezai and Allahkarami, 2021).

In cases where the population density is not high and conventional treatment plants cannot be built by making high-cost investments, natural treatment systems are constructed with low investment costs and without negative impacts on the environment. These systems generally serve small communities. Natural treatment systems called constructed wetlands, are similar to natural wetlands and imitate the ongoing processes of natural wetlands (Gökalp and Tas, 2018). Artificial wetlands are used as low-cost and sustainable wastewater treatment systems, especially in rural areas. For the removal of phosphorus, which is the primary source of pollution in domestic wastewater, the adsorption capacity of the filler material plays a critical role (Akçakoca and Gökalp, 2020).

Constructed wetlands contain plants and soil (filter material) to treat wastewater (EPA, 1993). They are commonly used for the treatment of industrial, agricultural, and domestic wastewater (Dombush, 1989; Du Bowry and Reaves, 1994; Riviera et al., 1997; Trautmann et al., 1989; Cooper et al., 1997; Schreijer et al., 1997).

Zeolites are hydrated aluminum silicates in crystalline structures originating from volcanic rocks. They contain discontinuous micropores and are widely used as adsorbents and catalysts (Chmielewská, 2014; Anonymous, 2022). Zeolites are used as soil stabilizers, fertilizer additives, water retainers, and soil aerators in agriculture, as a growing medium in plant production, in landscaping and gardening, as feed additive and animal bedding material in livestock operations, as mechanical and chemical filters in treatment, in holding toxic wastes, as filter material in pools and spas, in aquariums, as cat litter, in cleaning materials, textile, paper and energy industries, in health sector, as a catalyst in aquaculture and chemistry. They also have a wide range of uses in waste and utility water treatment (Çeğin and İmamoğlu, 2005; MTA, 2021).

Paddy farming is practiced by over 1.3 million decares in Türkiye, and annual production is about 1 million tons. While 600 thousand tons of this production is rice, the remaining 400 thousand tons emerge as husk, a waste material (TUIK, 2022). Rice husk is a kind of bio-waste mainly used as an adsorbent. Rice husk creates significant environmental problems in managing and disposing of agricultural wastes (Kalderis et al., 2008; Asadi et al., 2008).

Current research on constructed wetlands mainly focuses on better and more efficient filter or substrate materials for phosphorus and nitrogen removal from wastewater. Different materials have been tested, and porous materials are more successful in removing phosphorus and nitrogen from wastewater. In this study, filter column tests assessed the phosphorus and nitrogen removal performance of both zeolites, abundantly available in Türkiye, and rice husk, abundantly available waste material, from synthetic wastewaters.

MATERIALS AND METHODS

Zeolite and rice husk were used as adsorbent materials in column tests. Gördes Zeolite Co. supplied zeolite, and a local farmer supplied rice husk. The material size was selected as between 0.5 - 1.0 mm. Physico-chemical characteristics of zeolite and rice husk are provided in Table 1. Besides pure zeolite and rice husk, different mixtures (25:75, 50:50, and 75:25) of these materials were also used in the present experiments (Table 2).

Table 1. Physico-chemical characteristics of rice husk and zeolite

Rice Husk Property	Value	Zeolite Property	Value
SiO_2	90.89%	SiO_2	71.6%
Al_2O_3	0.93%	Al_2O_3	11.3%
CaO	1.25%	CaO	2.27%
Fe_2O_3	0.47%	Fe_2O_3	1.39%
K_2O_3	2.34%	K_2O	3.67%
MgO	0.81%	MgO	0.86%
Na_2O	-	Na_2O	0.86%
pH	6.5-7.5	pH	6.5–7.5
Moisture Content	8–12%	Moisture Content	8%
Water Retention Cap.	(105). %	Water Retention Cap.	75%

Table 2. Experimental treatments (mixture ratios, %)

Treatments	Rice Husk (%)	Zeolite (%)
100R	100	-
100Z	-	100
75R25Z	75	25
50R50Z	50	50
25R75Z	25	75

Column tests were conducted in glass pipes with a length of 60 cm and an internal diameter of 30 mm. Initially, substrate materials were placed into filter columns (100 cm^3). Substrate columns were saturated with phosphorus solutions (mono potassium phosphate) and nitrogen solutions (potassium nitrate) at different concentrations (0, 10, 25, and 50 mg L^{-1}). The synthetic solution of each concentration was passed through the column at flow rates of 5.0 mL min^{-1}. A peristaltic pump (Longer Pump brand) was used to adjust flow rates. Substrate columns were subjected to 3, 6, 12, 24, and 48 hours of hydraulic retention times. Effluent samples were taken at the end of each hydraulic retention time. Samples were then analyzed for pH, EC, phosphorus, and nitrogen concentration. Sample pH was measured using a Hanna-brand pH meter with a glass electrode. Sample EC was measured using an EC-meter (Hanna brand). Total phosphorus (TP) was measured using the ammonium molybdate blue color method in a spectrophotometer at 882 nm. Total nitrogen (TN) was measured using a nitrate-selective electrode (Hanna brand).

RESULTS AND DISCUSSION

Solutions containing different phosphorus and nitrogen concentrations (10, 25, and 50 mg L^{-1}) prepared under laboratory conditions were applied to the columns containing filter materials at a flow rate of 5 mL min^{-1}. Effluent samples were taken from column ends at 3rd, 6th, 12th, 24th and 48th hours. The samples obtained were subjected to pH, EC, total nitrogen (TN), and total phosphorus (TP) analyses.

pH Values

The pH values of effluent samples are given in Table 3. Initial pH levels of the solutions prepared at different concentrations (10, 25, and 50 mg L^{-1}) were determined as 5.70, 5.41, and 5.03, respectively. Effluent pH values varied between 6.20 (50 mg L^{-1}, 50Z50R) and 7.37 (10 mg L^{-1}, 25Z75R) at the end of the 3rd hour, between 6.13 (50 mg L^{-1}, 50Z50R) and 7.28 (10 mg L^{-1}, 100Z) at the end of the 6th hour, between 6.06 (50 mg L^{-1}, 100Z) and 6.88 (10 mg L^{-1}, 100R) at the end of the 12th hours, between 6.07 (50 mg L^{-1}, 75Z25R) and 6.96 (10 mg L^{-1}, 25Z75R) at the end of the 24th hour and between 6.01 (50 mg L^{-1}, 25Z75R) and 7.56 (10 mg L^{-1}, 50Z50R) at the end of 48th hour. According to the Water Pollution Control Regulation of the Ministry of Environment, Urbanization and Climate Change of the Republic of Turkiye, pH values of wastewater effluents should be between 6-10 (SKKY, 2004). Present pH values all comply with discharge criteria.

Table 3. Effects of mixture ratios on filtrate pH

Mixtures	Hydraulic retention times / Solution concentrations (mg L^{-1})														
	3 h			6 h			12 h			24 h			48 h		
	10	25	50	10	25	50	10	25	50	10	25	50	10	25	50
Zeolite	7.32	6.71	6.4	7.28	6.55	6.14	6.76	6.33	6.06	6.73	6.31	6.11	6.64	6.35	6.15
Rice Husk	6.92	6.48	6.35	6.9	6.43	6.33	6.88	6.42	6.27	6.72	6.38	6.24	6.68	6.25	6.22
75Z - 25R	7.05	6.84	6.49	7.02	6.57	6.35	6.82	6.44	6.13	6.68	6.25	6.07	6.63	6.24	6.06
50Z - 50R	6.88	6.52	6.2	6.8	6.44	6.13	6.77	6.41	6.11	6.87	6.36	6.09	7.56	6.33	6.08
25Z - 75R	7.37	6.54	6.23	6.8	6.42	6.16	6.82	6.45	6.12	6.96	6.48	6.1	6.9	6.49	6.01

EC (µS/cm) Values

The EC values of effluent samples are given in Table 4. Initial EC values of the solutions prepared at different concentrations (10, 25, and 50 mg L^{-1}) were determined as 116.5, 227.58, and 442.89 µS/cm, respectively. Effluent EC values varied between 139.20 (10 mg L^{-1}, 50Z50R) and 618.0 µS/cm (50 mg L^{-1}, 100R) at the end of 3rd hour, between 136.70 (10 mg L^{-1}, 75Z25R) and 579.90 µS/cm (50 mg L^{-1}, 100R) at the end of 6th hour, between 132.60 (10 mg L^{-1}, 75Z25R) and 580.60 µS/cm (50 mg L^{-1}, 100R) at the end of 12th hour, between 128.30 (10 mg L^{-1}, 100Z) and 602.60 µS/cm (50 mg L^{-1}, 100R) at the end of 24th hour and between 125.70 (10 mg L^{-1}, 75Z25R) and 559.30 µS/cm (50 mg L^{-1}, 100R) at the end of 48th hour. According to the Water Pollution Control Regulation of the Ministry of Environment, Urbanization and Climate Change of the Republic of Turkey, EC values of wastewater effluents should be <2000 µS/cm. Present EC values all comply with discharge criteria.

Table 4. Effects of mixture ratios on filtrate EC (mS/cm)

Hydraulic retention times / Solution concentrations (mg L^{-1})	Mixtures		Zeolite	Rice Husk	75Z - 25R	50Z - 50R	25Z - 75R
	3 h	10	144.6	153.4	147.8	139.2	210.7
		25	259.1	294.8	280.6	244.7	283.6
		50	455.6	618	486.5	490.4	535.4
	6 h	10	142.4	140.3	136.7	145.5	176.9
		25	252.8	282.4	261.1	249.2	280.9
		50	467.8	579.9	499	493.1	542.2
	12 h	10	146	172.8	132.6	165.2	154.6
		25	259.7	278.2	259.2	270.4	278.9
		50	498.6	580.6	512.2	510.2	544.9
	24 h	10	128.3	195.9	129.6	168.5	156.8
		25	272.6	288	272.7	277	283.1
		50	513.8	602.6	516.8	519.3	551.5
	48 h	10	213.2	132.5	125.7	173.6	216.5
		25	281.3	285.1	280.1	284.1	285.7
		50	546.9	559.3	524.1	525.7	555.8

Synthetic wastewaters were prepared using potassium nitrate (KNO3) and potassium dihydrogen phosphate (KH2PO4). Increasing phosphate and nitrate salt concentrations are expected to increase EC values. Therefore, it is important to carry out studies to increase the exchange capacity of materials to achieve more successful results.

TN (mg L^{-1}) Values

The TN values of effluent samples are given in Table 5. Effluent TN values varied between 2.49 (10 mg L^{-1}, 75Z25R) and 40.33 mg L^{-1} (50 mg L^{-1}, 50Z50R) at the end of 3rd hour, between 3.78 (10 mg L^{-1}, 75Z25R) and 45.73 mg L^{-1} (50 mg L^{-1}, 50Z50R) at the end of 6th hour, between 5.36 (10 mg L^{-1}, 75Z25R) and 48.36 mg L^{-1} (50 mg L^{-1}, 50Z50R) at the end of 12th hour, between 6.93 (10 mg L^{-1}, 75Z25R) and 48.90 mg L^{-1} (50 mg L^{-1}, 50Z50R) at the end of 24th hour and between 8.45 (10 mg L^{-1}, 75Z25R) and 49.65 mg L-1 (50 mg L^{-1}, 75Z25R) at the end of 48th hour. According to the Water Pollution Control Regulation of the Ministry of Environment, Urbanization and Climate Change of the Republic of Turkey, TN values of wastewater effluents should be < 100 mg L-1 (SKKY, 2004). Present TN values were all comply with discharge criteria.

Montalvo et al. (2011) applied an ammonium solution at a concentration of 100 ppm to zeolite and limestone and achieved 95% success. Lin et al. (2014) applied ammonium solutions at a concentration of 200 ppm to 300 g of zeolite material at a flow rate of 10 ml/min and achieved a success of up to 100%. Kumak (2022) applied nitrogen solutions at 10, 20, and 40 ppm concentrations to zeolite and pumice materials for 96 hours and achieved 58% removal efficiency in 50-50% mixtures of both materials. Karapınar (2009) applied ammonium solution at 10, 20, and 40 ppm concentrations to zeolite material for 90 minutes and achieved about 40% removal efficiency.

Table 5. Effects of mixture ratios on filtrate TN (mg L^{-1})

Hydraulic retention times / Solution concentrations (mg L^{-1})	Mixtures		Zeolite	Rice Husk	75Z - 25R	50Z - 50R	25Z - 75R
	3 h	10	2.57	4.48	2.49	3.09	3.05
		25	14.80	12.8	12.39	13.10	14.56
		50	35.46	37.33	31.50	14.56	38.10
	6 h	10	4.71	6.79	3.78	5.57	5.68
		25	19.23	14.86	14.92	14.90	18.3
		50	39.66	41.36	39.43	45.73	40.9
	12 h	10	6.13	7.78	5.36	8.35	6.60
		25	22.93	18.36	16.63	15.36	22.83
		50	43.46	45.26	42.46	48.36	43.13
	24 h	10	8.25	8.44	6.93	8.90	7.22
		25	23.03	22.36	19.71	16.73	23.43
		50	47.26	46.40	47.31	48.90	46.43
	48 h	10	9.20	9.26	8.45	9.35	8.98
		25	24.76	23.63	22.53	19.53	24.23
		50	49.53	48.53	49.65	49.50	48.26

TN Removal Performance (%)

Nitrogen removal performance (%) of different filter materials from wastewater was calculated. The nitrogen removal performance of the materials varied between 19.34% (50 mg L^{-1}, 50Z50R) and 75.10% (10 mg L^{-1}, 25Z75R) at the end of the 3rd hour, between 8.54% (50 mg L^{-1}, 50Z50R) and 62.20% (75Z25R) at the end of the 6th hour, 3.28% (50 mg L^{-1}, 50Z50R) to 46.40% (10 mg L^{-1}, 75Z25R) at the end of the 12th hour, between 2.20% (50 mg L^{-1}, 50Z50R) and 30.70% (10 mg L^{-1}, 75Z25R) at the end of the 24th hour and between 0.70% (50 mg L^{-1}, 75Z25R) and 15.50% (10 mg L^{-1}, 75Z25R) at the end of the 48th hour (Table 6). The 25Z75R mixture showed the highest nitrogen removal performance among the materials used in this study.

Present findings on nitrogen removal efficiencies comply with the findings of Lin et al. (2014), Karapınar (2009), Montalvo et al. (2011), and Kumak (2022).

Table 6. Nitrogen removal performance of substrate materials (%)

Hydraulic retention times / Solution concentrations (mg L^{-1})	Mixtures		Zeolite	Rice Husk	75Z - 25R	50Z - 50R	25Z - 75R
	3 h	10	74.3	55.20	69.50	69.10	75.10
		25	40.80	48.68	41.76	47.60	50.44
		50	29.08	25.34	23.80	19.34	37.00
	6 h	10	52.90	32.10	62.20	44.30	43.20
		25	23.08	40.56	40.32	40.40	26.80
		50	20.68	17.28	21.14	8.54	18.20
	12 h	10	38.70	22.20	46.40	16.50	34.00
		25	8.28	26.56	33.48	38.56	8.68
		50	13.08	9.48	15.08	3.28	13.74
	24 h	10	17.50	15.60	30.70	11.00	27.80
		25	7.88	10.56	21.16	33.08	6.28
		50	5.48	7.20	5.38	2.20	7.14
	48 h	10	8.00	7.40	15.50	6.50	10.20
		25	0.96	5.48	9.88	21.88	3.08
		50	0.94	2.94	0.70	1.00	3.48

TP Values

The TP values of effluent samples are given in Table 7. Effluent TP values varied between 8.06 (10 mg L^{-1}, 100Z) and 49.20 mg L^{-1} (50 mg L^{-1}, 100Z) at the end of the 3rd hour, between 8.64 (10 mg L-1, 100Z) and 49.65 mg L^{-1} (50 mg L^{-1}, 25Z75R) at the end of the 6th hour, between 8.90 (10 mg L-1, 75Z25R) and 49.77 mg L-1 (50 mg L^{-1}, 25Z75R) at the end of the 12th hour, between 8.44 (10 mg L^{-1}, 100Z) and 49.90 mg L^{-1} (50 mg L^{-1}, 25Z75R) at the end of the 24th hour and between 8.86 (10 mg L^{-1}, 100Z) and 49.93 mg L^{-1} (50 mg L^{-1}, 25Z75R) at the end of the 48th hour. According to the Water Pollution Control Regulation of the Ministry of Environment, Urbanization and Climate Change of the Republic of Turkey, TP values of wastewater effluents should be < 10 mg L^{-1} (SKKY, 2004). In this study, only 10 mg L^{-1} influent concentration met this criterion, and the other influent concentrations (25 and 50 mg L^{-1}) did not meet the discharge criterion.

Table 7. Effects of mixture ratios on filtrate TP (mg L^{-1})

Hydraulic retention times / Solution concentrations (mg L^{-1})	Mixtures		Zeolite	Rice Husk	75Z - 25R	50Z - 50R	25Z - 75R
	3 h	10	8.06	8.70	8.36	9.27	8.91
		25	23.59	23.88	23.07	23.44	23.61
		50	49.20	48.29	43.42	47.24	48.73
	6 h	10	8.64	9.35	8.80	9.35	9.35
		25	23.52	24.07	22.72	24.43	24.30
		50	49.31	48.76	45.74	48.99	49.65
	12 h	10	8.99	9.43	8.90	9.42	9.55
		25	23.13	24.33	22.24	24.60	24.67
		50	48.01	49.44	47.67	49.13	49.77
	24 h	10	8.44	9.68	8.97	9.50	9.63
		25	23.66	24.67	22.09	24.65	24.69
		50	47.68	49.38	48.59	49.64	49.90
	48 h	10	8.86	9.92	9.37	9.62	9.85
		25	24.17	24.80	21.88	24.96	24.89
		50	47.44	49.82	49.05	49.87	49.93

Ping et al. (2008) applied phosphorus at a concentration of 1.5 ppm to zeolite material for 24 hours and achieved 95% removal efficiency. Montalvo et al. (2011) applied phosphorus solution at 40 ppm concentration to zeolite and limestone and achieved 67% success in phosphorus removal. Uzun et al. (2021) applied phosphorus solutions at 10, 20, and 40 ppm concentrations to sand, pumice, and zeolite materials for 96 hours and achieved an average of 90% success. Vera et al. (2014) applied a phosphorus solution at a concentration of 100 ppm to a 12-liter volume of zeolite material and determined a removal efficiency of up to 50% after one year. Lin et al. (2014) applied phosphorus solutions at a concentration of 400 ppm to 300 g of zeolite material at a flow rate of 10 ml/min and achieved a success of up to 100%. Jiang et al. (2013) applied phosphorus solution at two ppm concentrations to zeolite and iron sponges for 48 hours, achieving an average of 90% success. Karapınar (2009) applied a phosphorus solution at 10, 20, and 40 ppm concentrations to zeolite material for 90 minutes and determined approximately 40% removal efficiency. Shi et al. (2019) applied a solution containing 10 ppm phosphorus to zeolite material at a flow rate of 22.5 ml/min for 360 minutes and determined 70% removal efficiency.

TP Removal Performance (%)

Phosphorus removal performance (%) of different filter materials from wastewater was calculated. The phosphorus removal performance of the materials varied between 1.60% (50 mg L^{-1}, 100Z) and 19.40% (10 mg L^{-1}, 100Z) at the end of 3rd hour, between 0.70% (50 mg L^{-1}, 24Z75R) and 13.60% (10 mg L^{-1}, 100Z) at the end of the 6th hour, between 0.46% (50 mg L^{-1}, 2575R) and 11.04% (25 mg L^{-1}, 75Z25R) at the end of the 12th hour, between 0.20% (50 mg L^{-1}, 25Z75R) and 15.60% (10 mg L^{-1}, 100Z) at the end of the 24th hour and between 0.14% (50 mg L^{-1}, 25Z75R) and 12.48% (25 mg L^{-1}, 75Z25R) at the end of the 48th hour (Table 8). In this study, while 100Z yielded quite a high removal efficiency at an influent concentration of 10 mg L^{-1}, a 25% rice husk mixture increased the effect of material at higher concentrations.

Table 8. Phosphorus removal performance of substrate materials (%)

Hydraulic retention times / Solution concentrations (mg L^{-1})	Mixtures		Zeolite	Rice Husk	75Z - 25R	50Z - 50R	25Z - 75R
	3 h	10	19.40	13.00	16.40	7.30	10.90
		25	5.64	4.48	7.72	6.24	5.56
		50	1.60	3.42	13.16	5.52	2.54
	6 h	10	13.60	6.50	12.00	6.50	6.50
		25	5.92	3.72	9.12	2.28	2.80
		50	1.38	2.48	8.52	2.02	0.70
	12 h	10	10.10	5.70	11.00	5.80	4.50
		25	7.48	2.68	11.04	1.60	1.32
		50	3.98	1.12	4.68	1.74	0.46
	24 h	10	15.6	3.20	10.30	5.00	3.70
		25	5.36	1.32	11.64	1.40	1.24
		50	4.46	1.24	2.82	0.72	0.20
	48 h	10	11.40	0.80	6.30	3.80	1.50
		25	3.32	0.80	12.48	0.16	0.44
		50	5.12	0.36	1.90	0.26	0.14

Present findings on phosphorus removal efficiencies comply with the findings of previous studies. It was determined that the findings obtained from the study showed similar results to previous studies (Lin et al., 2014); Karapınar, 2009; Montalvo et al., 2011; Kumak, 2022). Differences were mainly attributed to influent concentrations, filter materials, and sampling times.

CONCLUSION

In present column tests, different concentrations (10, 25, and 50 mg L^{-1}) of phosphorus and nitrogen-containing synthetic wastewaters were applied to zeolite, rice husk, and mixtures of these materials (25% - 75%, 50% - 50%, and 75% - 25%) for 48 hours and effluent samples were taken at the end of 3rd, 6th, 12th, 24th and 48th hours. Present findings revealed that effluent pH, EC, and TN values were at desired levels after treatment and met the discharge criteria specified in Water Pollution Control Regulations. However, TP values met relevant criteria only at 10 mg L^{-1} influent concentration and did not meet the criteria at higher concentrations. Present findings revealed that zeolite had quite a high nitrogen removal efficiency, and rice husk further improved the nitrogen removal efficiency of zeolite. Zeolite was also highly efficient in phosphorus removal from wastewater, especially at low concentrations and flow rates.

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Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions

***1st* Yusuf Can *Aşık*:** formal analysis; investigation; writing— original draft; writing—review and editing.

2st Hasan Ali İrik : Conceptualization; data curation; funding acquisition; methodology; project administration; software; writing— original draft; writing—review and editing.

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