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A review on pumice for water and wastewater treatment

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ABSTRACT

Pumice is a valuable scouring, scrubbing, and polishing material both in powdered form and as a pumice stone. It has been traditionally used in construction industry and biomedicine. It has been evaluated in recent years in the field of water, wastewater, and air treatment. The present study aimed to review the scientific literature of pumice stone with the particular focus on its use for the treatment of water and wastewater. It was observed that most of the publications from 1995 to 2015 dealt with construction materials and treatment use. A number of 143 papers published focused on the removal of cadmium, dyes, color, and many other pollutants by adsorption and catalytic oxidation, while 49% of the papers on water and wastewater treatment was dedicated on adsorption processes. Besides, pumice has been used as a filter medium and integrated to biological treatment. More recent publications have been focusing on integrating pumice with advanced oxidation processes (AOPs) after enrichment with other materials. The use of pumice in AOPs, in particular, integrated with nanotechnology has been attracting more scientists to remove micropollutants.

Keywords: Pumice stone; Water and wastewater treatment; Adsorption; Advanced oxidation processes; Nanotechnology

1. Introduction

Porous and amorphous properties of pumice create large surface area and skeleton structure that contain open channels for water and ions to travel into and out of the crystal structure [1]. It is formed when volcanic gases exsolving from viscous magma nucleate bubbles, which cannot readily decouple from the viscous magma prior to chilling to glass [2]. Pumice is the highest porous material which is known with an average porosity of 90% and initially floats on water also, containing –OH groups is important for surface activity [2,3]. According to scanning electron microscopy (SEM), porous and rough surface of pumice can be further increased with chemical modification [4,5]. Fig. 1 displays SEM of a pumice from Turkey [6]. Its surface shows irregular texture with grains and edges in accordance with the literature (Fig. 1) [1–5].

Pumice can be abundantly found in the Mediterranean area (Italy, Turkey, Greece, and Spain), on the Rocky Mountains, and on the Pacific Coast of the USA [7]. Pumice mainly consists of SiO_2 as seen in Table 1 that shows characteristics of pumice from different locations mostly in Turkey and also around the world. Pumice stone also contains other essential compounds in the range of 13.5–17.2% of Al_2O_3, 2.4–10% of K_2O and trace amounts of TiO_2, CaO, MgO, and

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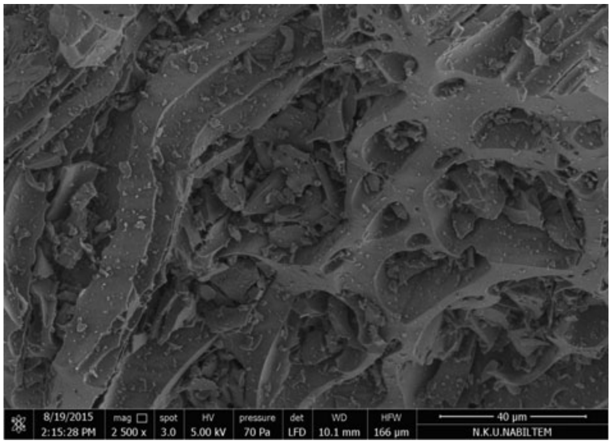

Fig. 1. SEM images of pumice [6].

Na_2O. Containing high proportion of silica caused the negatively charge on pumice surface and it could easily adsorp heavy metals [1].

Pumice has been used for centuries in the world for different purposes. Several industrial applications such as textile and detergents are well known. Furthermore, it has a good and low-cost adsorbent capacity as it has been reported to adsorb lots of metals, organics, and dyes [12,14]. Pumice surface ends with OH groups and oxygen bridges, which would perform as adsorption spots. Its surface principally comprises of oxygen, nitrogen, hydrogen, halogen, etc. Pumice is classified in two types which are acidic and basaltic characteristics. Acidic pumice contains higher SiO_2 than basaltic pumice. Furthermore, the density of acidic pumice is lower than the basaltic pumice. Because of these characteristic properties, acidic pumice is a more appropriate raw material and is used in construction material and as an adsorbent [15].

During the recent decades, scientific research related to environmental engineering has started to explore the use of pumice stone for waste, air, and water treatment using several properties such as adsorptive, dehydration, and catalyst characteristics of pumice [5,8–30]. Adsorption process has become the most studied one to remove metals, organic matter, dyes, etc. [2,5,8,31–41]. Recent investigations focused on integrating pumice stone to advanced oxidation processes (AOPs) such as ozonation and photocatalysis after supporting its surface by coating or doping metals with the purpose of increasing its catalytic capacity [4,9,14,42–46].

This work focused on an intensive review of the use of pumice stone in environmental engineering applications, particularly, for water and wastewater treatment. A particular interest is paid to explore the methods to increase the integration of pumice stone to AOPs [42–46].

2. Overview of application fields of pumice stone

Pumice is an important supported material that has been used in different applications. A wide variety of applications for pumice derivatives have been reported between 1995 and 2015 as summarized in Fig. 2. It can be seen that the number of scientific literature related to the use of pumice stone mainly as a building construction material and as materials of absorbent, filter aid to support water, wastewater and air treatment as well as waste treatment and hydrogenation processes, significantly increased during the

Table 1
Chemical composition of the natural pumice

Component	Sepehr et al. [8]	Kitis et al. [9]			Álvarez-Galván et al. [10]	Farizoglu et al. [11]	Akbal [12]		Pazarlioğlu and Telefoncu [13]
		Nevşehir	Kayseri	Isparta			Nevsehir	Kayseri	
SiO_2	63.45	74.1	68.5	59.0	52.5	72.07	70.35	63.00	74.0
Al_2O_3	17.24	13.5	14.9	16.6	19.7	13.5	14.60	16.25	15.6
TiO_2	0.37	0.07	0.2	0.6	–	0.35	0.15	0.75	–
P_2O_5	0.21	–	–	–	–	–	–	–	–
CaO	3.22	1.2	2.9	4.6	2.1	–	0.80	2.65	–
Fe_2O_3	2.86	1.4	3.1	4.8	3.7	1.21	1.5	3.30	–
SrO	0.09	–	–	–	–	–	–		–
MgO	1.03	0.4	0.95	1.8	3.5	–	0.10	0.80	–
K_2O	2.16	4.1	2.8	5.4	10.2	–	4.40	3.30	2.4
SO_3	0.16	–	–	0.4	–	–	–	–	–
Na_2O	2.00	3.7	4.1	5.2	8.3	11.27	3.60	3.70	2.4

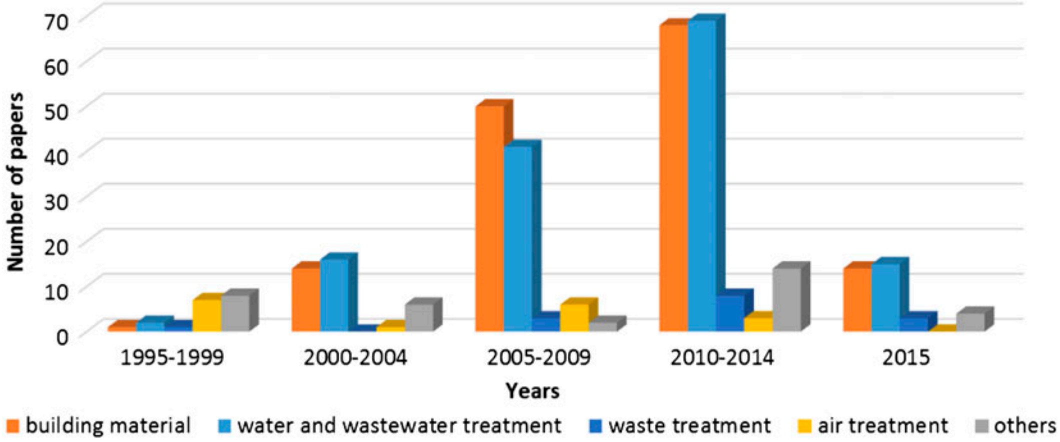

Fig. 2. Exploitation of pumice stone used in different sectors since 1995.

last decades. Use of pumice stone as a support medium in the environmental engineering applications has been progressively popular since 2005 and sharply increased between 2010 and 2015. According to the screening of 198 SCI and SCI-Expanded-indexed papers between 2010 and 2015 years,about 41% portion was dedicated to building materials, while 50% portion was related to the field of environmental engineering. Waste treatment studies focused on better composting process and increasing the compost quality [18,19,47–49].

3. Application of pumice stone to water and wastewater treatment

As can be seen in Fig. 2, 49% of scientific publications were dedicated to adsorption processes. In other terms, a total number of 143 papers published in the field of water and wastewater treatment focused on the removal of cadmium, dyes, color, and the catalytic degradation of p-chloronitrobenzene in the presence of ozone, phenol and 4-chlorophenol, water softening, and so on [45,50,51]. Pumice stone was used successfully as an adsorbent for the removal of heavy metals such as As, Ar, Cu, Co, Ce, Zn, Se, Cd, Cr, and Ni [24,26,28–30,39,52–63], radioactive metals such as Sr, Cs, U, and Th ions [64–67], and dyes [15,37,41,68–74] from wastewater.

About 21% portion of scientific publications dealt with the use of pumice stone in biological treatment as a carrier medium [75–81]. And 9% of the other papers published included studies on the synthesis and characterization and metal-doped pumice to increase its density.

3.1. Incorporation of pumice to adsorption process

Pumice porous structure is important for the adsorption mechanism over the surface, and pore of pumice and the main adsorption mechanisms involved in the removal process are hydrogen bonding, electrostatic, and n–p interactions [37]. In recent years, adsorption and oxidation studies have been progressing by doping metals (such as Fe, Al, Mg, and Cu) on pumice or modifying pumice with acidic or basic pH values to enhance adsorption capacity of pumice stone and to increase decolorization efficiency [1,5,8,62,82–85]. In the literature, different kinds of modification methods have been used on adsorbent such as base solutions (sodium hydroxide, calcium hydroxide, and sodium carbonate), minerals and organic acid solutions (hydrochloric acid and nitric acid), and oxidizing agent (hydrogen peroxide). The natural pumice was mainly pretreated with 1-M HCl (or pH was set 1 with HCl) for 24 h for purification due to the containing residual inorganic salts and acid-soluble contents [5,8,9,14,25,28,43,83]. Kitis et al. have produced iron and copper-doped pumice by putting metal and acid-treated pumice with HCl into the distilled water, adjusting pH of 9.5 (with 3 M NaOH), stirring for 30 min, and finally, doped pumice was dried at 80˚C for 24 h and 50˚C for 72 h [9,14,25,43]. Sepehr et al. produced alkaline modified pumice by stirring 2-M NaOH for 24 h at room temperature, while $MgCl_2$ supported pumice was produced by stirring pumice with 2-M $MgCl_2/H_2O_2$ (30%v/v) solution [5,8,83]. To increase pumice adsorption capacity, pumice was also modified by chitosan [60]. Acid-treated pumice and chitosan were mixed in oxalic acid for 2 h at the same mixing temperature, neutralized by NaOH solution, and dried at 60˚C [60].

Asgari et al. studied the effects of cationic surfactant (hexadecyltrimethyl ammonium)-modified pumice for the removal of fluoride from drinking water [2]. The results showed that surfactant-modified pumice exhibited the best performance, as 41 mg/g of the maximum amount of adsorption at dose 0.5 g/L, pH 6, and 96% of fluoride removal was obtained from a solution containing 10-mg/L fluoride with 30 min adsorption time. Salifu et al. also investigated fluoride removal using aluminum oxide-coated pumice with 1.5–5.0 mg/L initial fluoride concentrations and 1 h adsorption time [40]. Sepehr et al. found that magnesium chloride modification and hydrogen peroxide modification of pumice improved the removal efficiency of fluoride and the fluoride removal increased from 65.4 to 70.8% by magnesium chloride modification and hydrogen peroxide modification of pumice [5]. Chromium adsorption by pumice depends significantly on the solution pH due to the main chromium species such as $HCrO_4^-$, $Cr_2O_7^{2-}$, and H_2CrO_4 in the acidic conditions. Maximum Cr(VI) sorption capacities of natural pumice and $MgCl_2$ modified pumice were obtained as 87.72 and 105.26 mg/g at optimum pH 1, respectively [8].

Modification of natural pumice with magnesium increased the specific surface area of pumice and enhanced phosphorus adsorption from 69 to 97% [84]. Most of the research performed in the scientific literature encourages the use of pumice for heavy metal adsorption [24,26–30,39,52,53]. Furthermore, results of the study on nano zero-valent iron (ZVI)—pumice combination showed that the nZVI particles provided much more reaction sites for heavy metals [1]. Comparing to natural pumice, iron oxide coating of pumice significantly enhanced dissolved organic carbon uptakes and decreased disinfection byproduct formation after chlorination [31]. Liu et al. prepared pumice-supported nZVI using ferric ion ($FeCl_3{\cdot}6H_2O$), sodium borohydride ($NaBH_4$), and pumice by stirring and ultrasound [1,62]. After saturation or doping of metals onto the pumice, these materials were washed with distilled water several times and dried at different temperatures (50–105˚C) and times (12–36 h) for calcination [1,24,26,28–30,39,52,53,62,82].

Reuse of adsorbent and regeneration are the important subjects for the adsorption process due to economical feasibility and also understanding the stability of modified pumice [5,8,83,84]. Fe^{3+} and Cr^{3+} precipitation were provided by washing nZVI-pumice with dilute HCl solution and 96, 77, 57, and 46% of Cr are removed for the first, second, third, and fourth times used [1]. When different pumice regeneration methods were compared, 9.3, 82.0, 94.3, and 63.0% regeneration yields were obtained using deionized water, 1 M H_2SO_4, 1 M HCl, and 4 N NaOH for pumice modification after 300 min contact time [8]. However, the regeneration method yields could be different for modified pumice than the pumice alone due to the different pH activity of doping metals. It is found that maximum regeneration yield was obtained to be 94.3% at acidic condition for natural pumice regeneration while it was found to be 91.3% at basic condition for $MgCl_2$ modified pumice [8]. For regeneration, saturated natural and modified adsorbents were stirred in phosphorous solution (pH: 6.5; 15 mg/L) at 200 rpm and 510 min and 22, and 96% regeneration were provided for natural and $MgCl_2$ modified pumice [84]. Maximum regeneration on natural and alkali (NaOH) modified pumice was obtained to be 99 and 92%, respectively, for Ca adsorption and 100 and 89%, respectively, for Mg adsorption after 510 min using NaOH solution [5].

Table 2 presents the results of kinetics evaluation of different isotherm models of pumice and modified pumice for the removal of various pollutants. Data shown in Table 2 indicate that pumice has been proven to be very effective in the removal of metals such as Cr and Hg. Also, pumice particle size is important for both pumice and modified pumice to have effective adsorption and high Cu and Zn removal efficiencies which were obtained at low particle size in both pumices [88].

3.2. *Pumice as a carrier medium for biological processes*

Pumice was used as a carrier medium for anaerobic and aerobic treatment in different wastewaters such as textile and sugar industry [75,76,89–97]. Garcia et al. found that comparing with polyurethane foam, vegetal carbon, and recycled low-density polyethylene, the highest apparent kinetic constants were obtained with pumice supported bed in an anaerobic sequencing batch biofilm reactor (AnSBBR) [75].

About 97.5% COD reduction and 99.5% decolorization were obtained in a microaerophilic fixed film reactor using pumice stone as a support material [76]. Biohydrogen production significantly increased by immobilized pumice-packed materials than CSTR type bioreactor in thermophilic conditions [89]. The formaldehyde and COD removal efficiencies were obtained at 97 and 88%. Pumice-packed bed bioreactors and pumice showed an efficient growth and attachment on biofilm [90]. The maximum adsorption of immobilized fungal biomass was obtained using pumice compared to other biosorbents [91].

Table 2
Isotherms and kinetics for adsorption of various contaminants by pumice and modified pumice from aqueous solutions

		Adsorption Capacity	Langmuir				Freundlich			Temkin			
Adsorbent	Contaminant	q_m (mg/g)	q_e (mg/g)	b (L/mg)	R_L (L/mg)	R^2	k_f (mg/g)(L/mg)	n	R^2	k_T (L/g)	b_1 (kJ/mol)	R^2	Refs.
Hydroxyapatite/ pumice	Tetracycline	17.87	17.87	0.0471	0.18	0.98	2.59	2.78	0.98				[87]
Pumice	RB 5	12.85	1.67–4.65	0.077	0.999	0.85							[37]
Pumice	Methylene blue						0.211–1.613	0.201–0.509	≥0.98				[70]
Pumice	Acid Orange 7		15.56	0.031	0.177	0.98	1.512	2.21	0.99				[74]
Fe-Pumice	Acid Orange 7		27.68	0.063	0.096	0.96	4.092	2.41	0.99				
Pumice	Crystal violet						0.118–0.772	0.402–0.495	0.96				[70]
Pumice	Phosphorous	11.88	11.88	2.37	0.08–0.2	0.97	6.16	0.75	0.99	14.03	65.02	0.94	[84]
$MgCl_2$ mod. pumice	Phosphorous	17.71	17.71	5.3	0.13–0.32	0.97	9.53	0.63	0.99	24.36	73.63	0.96	[84]
Surfactant mod. Pumice	Fluoride	41	39–42	0.25–0.26	0.16–0.17	0.99	27.6	3.2	0.95	1.618	32.46	0.95	[2]
Pumice	Cr(VI)	87.72	87.72	0.13	–	0.99	12.8	2.25	0.96	4.1	186.3	0.97	[8]
$MgCl_2$ mod. pumice	Cr(VI)	105.43	105.26	0.4	–	0.99	25.87	2.64	0.97	26.2	195	0.92	[8]
Pumice	Calcium	57.27	62.34	2.23		0.96	7.23	0.263	0.99	0.8	68.31	0.91	[83]
Alkaline mod. pumice	Calcium	62.34	57.27	1.33		0.91	9.24	0.357	0.996	1.69	82.44	0.94	[83]
Pumice	Magnesium	44.53	44.53	0.965		0.96	7.9	0.384	0.99	0.53	109.03	0.91	[83]
Alkaline mod. pumice	Magnesium	56.11	56.11	1.21		0.95	7.35	0.294	0.99	0.66	79.02	0.91	[83]
HDTMA-pumice	Phenol						0.0269	0.9792	0.99				[12]
HDTMA-pumice	4-chlorophenol						0.5270	0.5356	0.99				[12]
BDTDA-pumice	Phenol						0.0400	0.7298	0.99				[12]
BDTDA-pumice	4-chlorophenol						0.4853	0.4455	0.99				[12]
Pumice	Cadmium		5.28	0.00418		0.99							[30]
Pumice	Cr(III)		0.031–0.045	364–459		≥0.97	0.073–0.131	3.175–4.739	≥0.91				[26]
Pumice	Cr(IV)		0.079–0.086	108–234			0.518–0.584	1.755–2.003	≥0.89				[26]
Pumice	Cu(II)		0.055	614	0.619	0.99	0.811	1.808	0.95				[28]
Pumice	Cr(III)		0.031	1991	0.334	0.99	0.072	5.208	0.92				[28]
PAn/Pumice	Cu(II)		0.065	666	0.600	0.99	0.602	1.948	0.94				[28]
PAn/Pumice	Cr(III)		0.268	132	0.883	0.96	3.872	0.490	0.80				[28]
AOC pumice	Fluoride	7.6	11.82	0.057	0.7812	0.53				0.860	2.64	0.96	[40]
Pumice	Fluoride		4.525	0.219	0.19–0.48	0.85	0.521	2.554	0.98	1.712	19.82	0.97	[6]
HMP Pumice	Fluoride		11.765	0.173	0.22–0.54	0.87	0.535	2.273	0.89	1.162	18.04	0.72	[6]

(*Continued*)

Table 2 (*Continued*)

Adsorbent	Contaminant	Adsorption Capacity	Langmuir				Freundlich			Temkin			Refs.
		q_m (mg/g)	q_e (mg/g)	b (L/mg)	R_L (L/mg)	R^2	k_f (mg/g)(L/mg)	n	R^2	k_T (L/g)	b_1 (kJ/mol)	R^2	
MGMP Pumice	Fluoride		5.556	0.285	0.22–0.41	0.84	0.777	1.616	0.95	1.079	12.88	0.82	[6]
ZVI pumice	Hg(II)	107					104–174	2.73–4.81	≥0.96				[62]
ZVI pumice	Cr(IV)	107					81–131	2.49–5.16	≥0.97				[62]
Pumice	Cd(II)		3.84	5.7	0.67	0.99	53.6	1.67	0.99				[86]
Pumice	NOM						0.43	0.75					[14]
Fe Pumice	NOM						1.11	0.45					[14]

Adsorbent	Contaminant	Conc. (mg/L)	Pseudo-first order model				Pseudo-Second order model				Intra particle diffusion model				Refs.
			$q_{e,exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e,exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	K_2 (mg/g min)	R^2	k_{ip} (mg/g min)	Dp (x10^{-6})	D_F (x10^{-8})	R^2	
Hydroxyapatite/pumice	Tetracycline	10–300		3.15	0.028	0.921		7.87	0.026	0.99					
Pumice	RB 5	20–60	5.5	5.09	0.001	≥0.75		5.52	0.08	0.99	0.21				[37]
Pumice	Methylene blue							0.44–1.49	3.982–8.052	0.99					[70]
Pumice	Crystal violet							0.35–1.34	7.54–17.36	0.99					[70]
Pumice	Phosphorous	5–15	0.2–0.8	0.14–0.75	0.18–0.24	≥0.97	0.2–0.8	0.15–0.82	0.2–1.54	0.98	0.01–0.05	2.4–3.1	6.6–11	≥0.90	[84]
$MgCl_2$ mod. Pumice	Phosphorous	5–15	0.5–2.1	0.51–2.06	0.28–0.32	0.98	0.5–2.1	0.54–2.14	0.23–0.85	≥0.98	0.02–0.08	2.6–4.2	1.01–89	≥0.91	[84]
Surfactant mod. pumice	Fluoride						19.15	19.3	0.081	0.99					[2]
Pumice	Cr(VI)	10–100	1.0–13.6	1.0–13.7	0.008–0.011	≥0.95	1.0–13.6	1.29–16.83	0.013–0.018	≥0.98	0.04–1.26	2–3.75	3.16–5.3	–	[8]
$MgCl_2$ mod. Pumice	Cr(VI)	10–100	1.3–15.5	1.3–15.5	0.012–0.02	≥0.91	1.3–15.5	1.52–17.73	0.017–0.023	0.99	0.14–0.93	3.2–4.0	5.6–15	–	[8]
Pumice	Calcium	50–100					5.3–15.8	5.59–16.05	0.63–0.73	≥0.98					[83]
Alkaline mod. pumice	Calcium	50–100					5.9–23.5	6.30–25.70	0.71–0.89	≥0.97					[83]
Pumice	Magnesium	50–100					2.3–12.3	2.61–14.49	0.57–0.61	≥0.97					[83]
Alkaline mod. pumice	Magnesium	50–100					4.3–18.3	5.77–21.83	0.60–0.65	≥0.97					[83]
Pumice	Cadmium	3.4–13.5						0.06–0.19	0.006–0.007					[30]	
AOC pumice	Fluoride			0.102	0.00053	0.97		0.458	0.02657	0.99	0.00022			0.95	[40]
Pumice	Fluoride	5–20		0.39–1.70	2.31–2.92	≥0.95		0.57–2.87	3.32–7.63	0.99	3.73–16.45		≥0.81	[5]	
HMP Pumice	Fluoride			0.42–1.81	1.32–2.64	≥0.85		0.66–3.04	3.35–10.02	0.99	4.12–16.21		≥0.82	[5]	
MGMP Pumice	Fluoride			0.54–1.55	2.34–2.83	≥0.95		0.68–2.92	3.74–6.92	0.99	4.43–15.61		≥0.81	[5]	
ZVI pumice	Hg(II)	60			0.13–0.32	0.99									[62]
ZVI pumice	Cr(IV)	60			0.13–0.30	0.98									[62]
Pumice	Cd(II)						35–183	34.5–200	0.06–8.4	0.99					[86]

Table 3
Coating material of pumice stone for advanced oxidation of different environmental pollutants

Coating material	Treatment purpose	Remarks	Refs.
TiO_2-pumice on cement and TiO_2-pumice on polycarbonate	UV-A (300–450 nm) photocatalytic oxidation, reactor capacity 500 mL	~100% Acid Orange 7 (inital conc. 5.10^{-5} M) removal both material at 1.5 h irridation	[42]
		3-Nitrobenzenesulfonic acid (inital conc. 4.10^{-5} M) removal 95% TiO_2-pumice on cement and 50% TiO_2-pumice on polycarbonate at 7 h irridation in sunlight photoreactor	
	UV-A (300–450 nm) and sunlight photocatalytic oxidation	Treated textile wastewater 95–100% dye (UV_{260}) removal both material in UV-A at 3.5 h and ~95% dye (UV_{260}) and ~100% TOC removal both material in sunlight at 2.5 h	
Copper-impregnated pumice	Completely mixed batch reactor, catalytic oxidation, 100 mg/L initial cyanide concentration	Cyanide removal increased 20% with 1 g/L copper-impregnated pumice according to raw pumice after 24 h adsorption. Cyanide removal was obtained ~90% with 3 g/L copper-impregnated pumice and 150 mg/L H_2O_2 while it is 43% only H_2O_2 in 5 h adsorption. Max. cyanide removal was obtained at pH 8 and 20˚C temperature.	[9]
İron-coated pumice nanoparticles	Completely mixed batch reactors (CMBRs) in a temperature-controlled	10 and 59% NOM (UV280) removal and 22 and 49% DOC removal were obtained original pumice and iron-coated pumice, respectively	[14]
		50% NOM (UV280) removal were obtained with 3 g/L pumice and 1 g/L H_2O_2 concentrations and it increased to 90% NOM (UV280) removal with iron-coated pumice (16 mg Fe/g pumice)	
Pumice stone supported 30w% TiO_2	Sunlight photocatalytic oxidation	~100% Acid Orange 7 removal in 6.5 h, initial conc. 5.10^{-5} M	[44]
	Multi-tube reactor, sunlight photocatalytic oxidation	~100% *E. coli* inactivation in 90 min	
		83% TOC removal in 280 min, initial concentration of 4-nitro toluene-2-sulfonic acid is 6.10^{-4} M	
		60% TOC removal in 280 min, initial concentration of isoproturon is 1.94.10^{-4} M	
Pumice/TiO_2	Solar UV Simulator, TiO_2 = 1 g/L, Bezafibrate = 10 mg/L, pH 6.3)	Removal rate was obtained 0.20–0.25 at 1 h irridation time	[45]
Pumice and copper-coated pumice catalyzed ozonation	The pumice granules were modified by $CuSO_4$, Reactive Red 198 degradation	The removal efficiency of dye increased by increasing pH, contact time and catalyst dosages. The optimum conditions are 15 min reaction time, pH 8, copper-coated pumice dosages 10 g/L	[104]
Pumice-catalyzed ozonation	Catalytic ozonation of p-chloronitrobenzene (pCNB), initial pCNB is 100 μg/L and the catalyst is 1.0 g. 1.2 L flat-bottomed flask as the ozon reactor vessel	At pH 6.86, the rate constant of pumice-catalyzed ozonation increase 149% compared with ozonation alone. The rate constant of ozonation alone and pumice-catalyzed ozonation appeared to be decreased 73% and 194% with increasing of tert-butyl alcohol	[50]

(*Continued*)

Table 3 (*Continued*)

Coating material	Treatment purpose	Remarks	Refs.
Pumice-catalyzed ozonation		Compared with the cumulative effect of ozonation alone and adsorption of pumice, an increment of approx 26.5% of pCNB degradation was observed with the ozonation/pumice process and its decomposition rate increasing 1.374-fold and optimum pH was found 9	[51]
Pumice-supported zinc oxyhydroxide (ZMP) catalyzed ozonation	İnitial p-chloronitrobenzene (pCNB) is 100 μg/L and the catalyst is 1.0 g. 1.2 L flat-bottomed flask as the ozon reactor vessel	The pCNB decomposition rate increased 2.84-fold in the presence of ZMP compared with ozonation alone. pCNB is oxidized primarily by hydroxyl radicals (·OH) in ozonation/ZMP processes	[45]

Table 4
Comparison of chromium adsorption capacities and cost evaluation of different adsorbents (adopted from Babel and Kurniawan [107])

Adsorbents	Max. adsorption capacity (mg/g)	Optimum pH	Max. Cr(VI) Concentration (mg/L)	Adsorbant Dosage (g/L)	Time (h)	Commercial Price ($/kg)	($/kgCr$_{removed}$)	Refs.
Pumice	87.72	1	300	6	6	0.12–0.3	1.37–3.42	[8]
$MgCl_2$ mod. Pumice	105.43	1	300	6	6			[8]
ZVI mod. Pumice	107	3	60	1.1	1			[62]
Chitin	153.85	3	100	1	0.83	15–20	98–130	[109]
Chitosan	70.422	3	100	1	0.5	5–10	71–142	[109]
Chitosan	273	3	5	–	2	5–10	18–37	[110]
Chitosan	22.09	3	30	13	5	5–10	226–453	[110]
Non-cross-linked chitosan	78	5	1,000	3.3	2.67	5–10	64–128	[111]
Cross-linked Chitosan	50	5	1,000	3.3	2.67	5–10	100–200	[111]
Activated Alumina	25.57	3	50	10	3	1.5–3.5	59–137	[112]
Coconut shell charcoal	10.88	5	25	1.5	3	0.5–0.8	46–74	[108]
Commercial activated carbon	15.47	5	25	1.5	3	0.8–1.1	52–71	[108]
Activated Carbon (Filtrasorb 400)	145	2.5	1,000	4	10	20–22	138–152	[108,113]
Activated charcoal	12.87	2	20	5	2	1.0–1.1	77–86	[114]
Clinoptilolite	3.4	5	10	0.01	2	0.14–0.29	9–35	[115]
Bentonite	0.57	2	30	–	–	0.05–0.2	88–351	[116]

3.3. Pumice as a filter medium

Beyond the above-mentioned sectors, a 15% portion of the papers published, showed that pumice has been used in the field of filtration medium support [12,98–103]. According to sand filter incorporation data, pumice has a higher potential for use as a filter bed material for deep-bed sand filters to use in drinking water and wastewater treatment. Turbidity removal rates for sand and pumice were found to be 85–90% and 98–99% with the conditions of 750 mm bed depth, 7.64 m^3/m^2 h flow rate, and 0.5−1.0 mm grain size, respectively [11]. Pumice plus sand—gravel media filters also increased the filtration period according to the sand—gravel media filters as well [98].

3.4. Pumice as a catalyst in advanced oxidation process

During the recent years, there have been some studies to integrate pumice only or integrated use with AOPs. Those papers on AOPs applications compose of a 11% portion of all scientific papers published so far. Most of AOPs related papers focused on catalytic ozonation [45,50,51,104], catalytic oxidation [9,14,43], and photocatalytic oxidation process [42,44,105,106]. Table 3 overviews some of those investigations. The research results of using metal-doped pumice indicated that pumice is a very good support catalyst to improve the oxidation process efficiency. Specifically, it was concluded that immobilization of catalytic metals on pumice surface increased the oxidation capacity or decrease the oxidation process duration. Although pore structures and surface chemistry of pumice are more important for oxidation, the greatest advantage of pumice is that it has a higher surface area due to the porous structure [9,14,43]. Therefore, more of catalytic metals such as copper and iron was doped in active surface areas. While, pumice reduced UV absorbance (NOM) and DOC by about 10 and 22%, UV absorbance reduction and DOC removal from water increased to 59 and 49% with iron-coated pumice using hydrogen peroxide, respectively [14]. The use of copper-doped pumice with the addition of hydrogen peroxide significantly enhanced both the initial rate and extent of cyanide removal compared to the combined use of natural pumice with hydrogen peroxide [9,43]. At the same time, immobilization of TiO_2 on pumice surface was investigated in the literature [4,42,44,46]. According to study by Chuan et al. flotation of anatase-mounted TiO_2 pumice particles has gained more advantages than the other adsorbents. The adsorption capacity and photocatalytic activity were observed to be signifcantly increased [4]. In addition, TiO_2 was coated inside of the porous structure and this lead to a slight decrease in the photocatalytic activity of pumice after using it for several days [105].

Yuan et al. reported that pumice catalyst increased the degradation of p-chloronitrobenzene by 1.4-fold in the ozonation process in accordance with the previous literature [45,50,51]. The degradation of p-chloronitrobenzene increased by 2.8-fold when ozonation process was supported by zinc oxyhydroxide compared to the ozonation process performed alone [45]. The results indicated that the activity of pumice activity was relatively stable and that p-chloronitrobenzene removal decreased only from 84.3 to 80.6 after 10 times of being used [50]. Besides, Rahmani et al. observed a better degradation of Reactive Red 198 in a copper-coated pumice catalyst supported ozonation process than natural pumice catalyst supported ozonation process [104].

4. Cost evaluation

Chromium(VI) adsorption capacities and unit costs of some absorbents are summarized in Table 4. Based on the literature results shown in Table 4, it can be concluded that although chitin and chitosan showed maximum adsorption capacities, their prices are very high compared to other adsorbents. Additionally, activated carbon (Filrosorb 400) provided higher Cr(VI) adsorption capacity of 145 mg/g [107,113].

Among the adsorbents used to remove Cr, the price of pumice is the lowest (about 100 times cheaper than that of chitin, chitosan, and activated carbon). Thus, this fact makes pumice a very attractive adsorbent. On the other hand, the other cheapest adsorbents such as bentonite, clinoptilolite, and charcoal were found to have lower adsorption capacities of Cr(VI) and this causes to increase the operating costs due to the increasing amount of adsorbent used for the removal of Cr(VI). A 87.72 mg/g adsorption capacity of Cr(VI) by pumice could be increased up to 105–107 mg/g with its modification by $MgCl_2$ or ZVI [8,62]. Considering the above-mentioned factors as well as high porous structure resulting in the high specific surface areas makes pumice the most valuable among other adsorbents.

5. Conclusion and future outlook

Review of the scientific literature revealed that the use of pumice stone has gained more and more importance from 1995 to 2015 for different application purposes, mainly as a material for building sector and for water, wastewater, waste, and air treatment technology. Adsorption process composes the highest ratio of the research, with the particular focus on doping materials on pumice. The number of studies in this line are increasing and many efforts to develop new materials by increasing adsorption as well as catalytic capacity of pumice to be used in photocatalysis or combined to AOPs have already been attempted. However, the need to develop hybrid catalysts to further increase the catalytic activity of pumice seems to be obvious, in particular, as the nanotechnology is the emerging technology of future applications. It is recommended to increase such nanotechnology-supported studies to explore the improved catalysts capacity of pumice stone which is a natural raw resource for developing countries, like the case of Turkey, where pumice is abundant.

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