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TECHNICAL ARTICLE

Adsorption of Copper and Zinc Ions from Aqueous Solutions Using Montmorillonite and Bauxite as Low-Cost Adsorbents

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Abstract The objectives of this study were to investigate the adsorption of Cu-II and Zn-II on montmorillonite and bauxite and to discuss the usability of these adsorbents in environmental applications. The maximum adsorption was found for Cu (II) on bauxite with a Kf value of 4.179 L g^{-1}; the maximum adsorbed capacity (Q_o) calculated from the Langmuir model reached 9.115 mg g^{-1}. Both raw materials have the potential to be effectively used to produce low-cost sorbents for copper and zinc removal from wastewater. They could be used as alternative adsorptive barriers and as amendments to soils at old mining areas, to prevent metal leaching into groundwater, or to isolate urban waste leachate.

Keywords Metal contaminants · Adsorptive barriers · Remediation · Batch method · Isotherms

Introduction

Drainage from abandoned metal mines and mine wastes typically contains dissolved metals, such as iron, zinc, copper, aluminum, and manganese, which may be many orders of magnitude greater than nonpolluted water bodies (Hedrich and Johnson 2014). Metal sulfide minerals (MS) oxidize and dissolve, increasing metal (M^{2+}) and sulphate (SO_4^{2-}) concentration (Jennings and Dollhopf 1995; Sheoran and Sheoran 2006; Younger et al. 2002). Metals discharged into the environment can potentially be toxic to humans, animals, plants, and aquatic life (Bsoul et al. 2014).

Sorption is one of the key processes affecting the fate of metals in the sediment–water–soil environments. Adsorption of contaminants in the soil reduces their mobility and leaching potential (Atasoy 2008; Si et al. 2006). Clay-size particles, metal oxides, organic matter surfaces, and silicate clay interlayers are the dominant sites in soil responsible for the sorption of metals, so sand and sandy soils in mining areas that are low in clay or Al and Fe oxides have little metal adsorption potential. A complete understanding of the adsorption of each metal is needed to how metals are transported and attenuated in soils and aquifers (Gove et al. 2001).

Cost-effective approaches for the remediation of acid mine drainage (AMD) and contaminated groundwater are greatly desired (Gibert et al. 2013). Permeable barriers (PBs) can passively remediate groundwater and prevent groundwater contamination, even in extreme environments. The main component of a PB is a reactive or sorbent material. However, no single material can remove all types of pollutants. Therefore, a material (or materials) with the ability to remove the contaminants present at the site has to be selected when installing any PB system. Several materials such as zeolite, zero valent iron (Jung et al. 2013), fly ash, or clays are commonly used to construct PBs (Kozyatnyk et al. 2014). However, some important data, such as adsorption rates and capacities, optimum adsorbent

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dosages of materials and the effects of pH should be known to evaluate the best adsorbent to use.

The objectives of the research were to: (1) investigate the adsorption of copper (Cu-II) and zinc (Zn-II) ions on montmorillonite and bauxite, (2) study the applicability of montmorillonite and bauxite for the treatment of industrial wastewater or mine drainage water containing Cu (II) and Zn (II) and, (3) propose locally available and low cost-effective adsorbents, such as montmorillonite and bauxite, as alternative adsorptive barriers for porous soils in contaminated sites or old mining areas.

Because of its structural characteristics, montmorillonite has excellent adsorptive properties; it possesses adsorption sites within its interlayer space, a large surface area, and more narrow channels inside (Seliman et al. 2014). The soils in southeastern Turkey typically contain 60–65% clay; the dominant clay type is montmorillonite (Mermut et al. 1996).

Bauxite is also abundantly available in Turkey. It typically consists of alumina, iron, silica, and titanium oxides, with an aluminium content that usually ranges between 50 and 70% (Atasoy et al. 2013).

Materials and Methods

Purified montmorillonite was provided by the Soil Science Department of the University of Saskatchewan, Canada. Montmorillonite belongs to the 2:1 clay family and its basic structural unit is composed of two tetrahedral coordinated sheets of silica ions surrounding a sandwiched octahedral coordinated sheet of aluminium ions. The isomorphic substitution occurs in the tetrahedral layers by substitution of Al^{+3} for Si^{+4} and in the octahedral layer by substitution of divalent cation such as Mg^{+2} for Al^{+3}, which results in a net negative surface charge in the clay. The chemical composition of the montmorillonite is presented in Table 1. Based on its X-ray diffractogram, it contained calcian montmorillonite (28.6%), albite (15.1%), quartz (13%), and trioctahedral illite (8.1%) (Supplemental Fig. 1), with the rest being trace amounts of other materials and possibly some amorphous material.

The bauxite used in the present study was a local material procured from the Seydisehir aluminium process plant, Eskisehir, Turkey. It was air-dried and sieved (<2 mm) in the Geological Engineering Laboratories in Istanbul Technical University. The chemical composition of the bauxite is presented (Table 1). Based on its X-ray diffractogram, it consisted of 32.4% boehmite, 26% kaolinite, 24.1% calcite, and 21.1% hematite (Supplemental Fig. 2).

Batch adsorption tests were carried out on the optimum dosage of montmorillonite and bauxite using 50 mL polypropylene test tubes containing 25 mL test solutions with initial concentrations of 0.70, 3.87, 7.92, 24.12, 43.13, 44.03, 76.08, and 102.20 mg L^{-1} of Cu (II) and 0.70, 3.69, 8.09, 21.57, 32.54, 41.05, 73.77, and 86.49 mg L^{-1} of Zn (II). Equilibrium time, optimum adsorbent dosage, and adsorption isotherms were determined by adsorption tests at room temperature (25 °C). All of the experiments were executed along with controls, either without adsorbents, or blanks with the same amount of adsorbent, but without metals.

Table 1 Chemical composition of montmorillonite and bauxite

Chemical composition	Concentration %	
	Montmorillonite	Bauxite
SiO_2	58.416	8.888
Al_2O_3	17.165	53.823
Fe_2O_3	1.542	18.266
MgO	6.193	0.197
CaO	3.019	1.300
Na_2O	0.068	0.554
K_2O	0.188	2.667
TiO_2	0.232	0.027
P_2O_5	0.015	0.014
MnO	0.074	0.054
Cr_2O_3	–	14.210
LOI	13.090	100%
Total	100.000	100.000

A preliminary kinetic experiment established the equilibrium times for the 16 and 19 mg L^{-1} initial concentrations of Cu (II) and Zn (II), respectively. Adsorbents (0.25 g) were mixed with 25 mL of metal solutions (10 g L^{-1}) on a reciprocating shaker (150 rpm) for 15, 30, 45, 60, 120, 180, 240, 360, and 480 min to attain the equilibrium time at room temperature (25 °C) and then the supernatant was filtered through 0.45 µm syringe filters and analyzed for the Cu (II) and Zn (II) in an inductively coupled plasma (ICP) mass spectrometer (Perkin Elmer Optima 5300 DV model). All of the tests were conducted in duplicate. The specific amount of metal adsorbed and percent metal adsorption was determined by calculating the mass balance equation.

Stock solutions containing Cu (II) and Zn (II) were prepared from $CuSO_4 \cdot 5H_2O$ and $ZnSO_4 \cdot 7H_2O$ (Merck) in 1 L of deionized water. This was further diluted to get the desired concentration for practical use. Solutions of 0.1 M HCl and 0.1 M NaOH were used for pH adjustment. The pH was measured with a Jenway Model 370 pH meter. All solution samples were filtered and analyzed as described above. The adsorption data were analyzed using linearized forms of the Langmuir and Freundlich isotherms (Sparks 1995).

Results and Discussion

Figure 1 shows the effect of contact time on the adsorption of Cu and Zn on montmorillonite and bauxite. The adsorption of Cu and Zn ions was initially fast and gradually approached an almost constant value, denoting attainment of equilibrium. Over 95% of the Cu (II) and Zn (II) that adsorbed did so in 15 min; the changes in solute concentration were quite small after 60 min. Malarvizhi and Santhi (2013) and Bouhamed et al. (2014) have explained that this is due to the availability of adsorption sites and because adsorbed species may either block access to internal pores or cause adsorbent particles to aggregate. Because both the montmorillonite and bauxite attained equilibrium, an equilibrium time of 60 min was assigned in the remaining adsorption studies.

The percent adsorbed increased with the amount of both montmorillonite and bauxite (Fig. 2). This is presumably due to the increased availability of surface active sites with

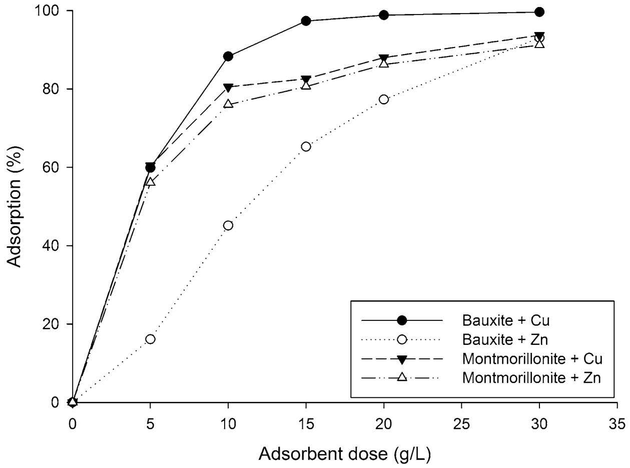

Fig. 2 Effect of adsorbent dose on the Cu and Zn adsorption

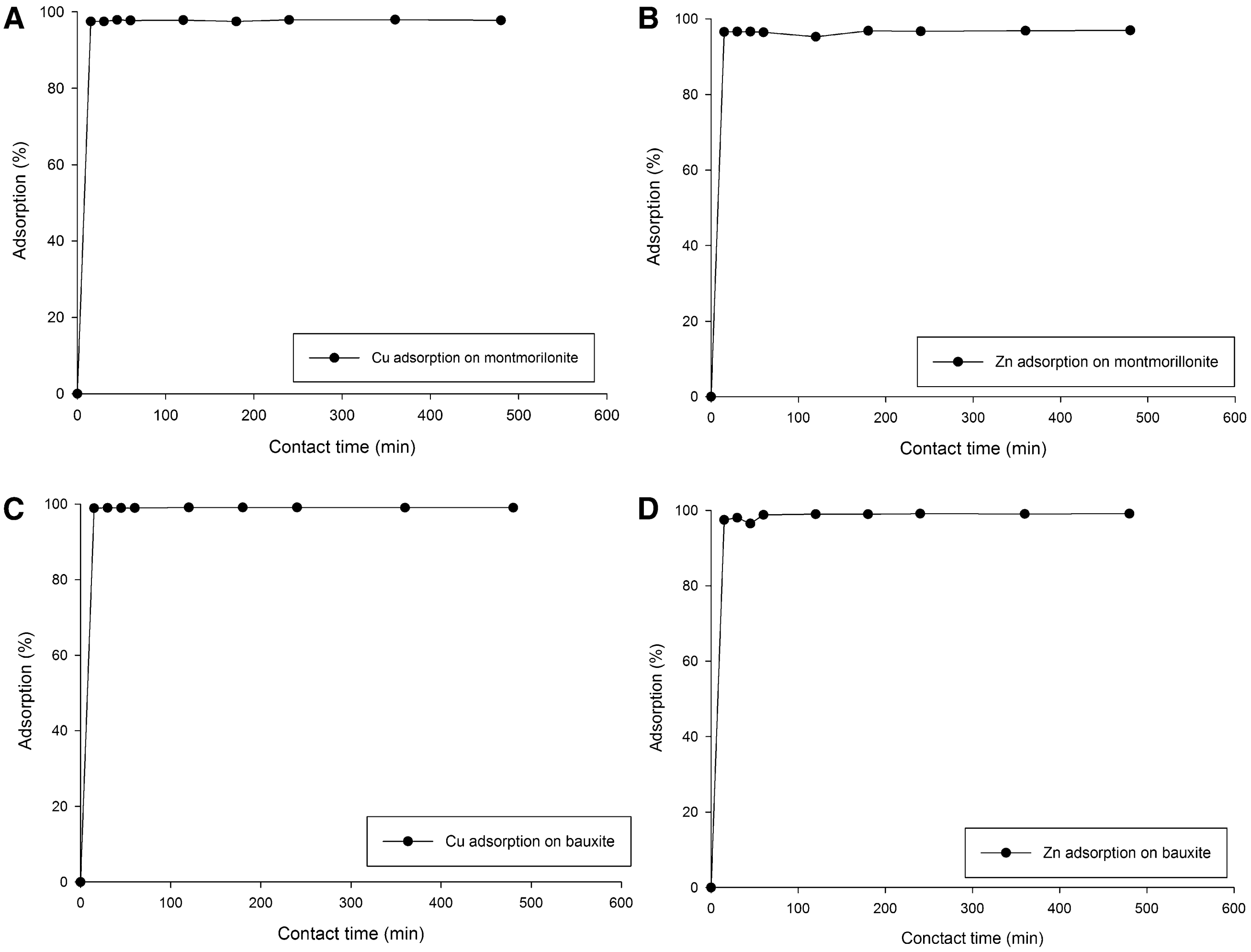

Fig. 1 Effect of contact time on the **a** Cu adsorption on montmorillonite, **b** Zn adsorption on montmorillonite, **c** Cu adsorption on bauxite and **d** Zn adsorption on bauxite

more adsorbent. The maximum adsorption percentage was achieved for 30 g L^{-1} of adsorbent for both the Cu and Zn. Further increasing the adsorbent dose did not effectively change the adsorption rate after a dose of 10 g L^{-1} except for Zn adsorption on bauxite, which continued to increase with the bauxite dosage. However, 10 g L^{-1} was fixed as the optimum dosage, considering cost-effectiveness, for both adsorbents.

The impact of the initial metal concentration on adsorption of Cu (II) and Zn (II) was also investigated by keeping other parameters constant such as adsorbent dose (10 g L^{-1}), shaking speed (150 rpm), and contact time (60 min). The effect of initial Cu and Zn concentration on the adsorption rate is shown in Figs. 3 and 4, respectively. Both Cu and Zn exhibited a declining adsorption tendency with increasing initial concentrations. This is thought to be due to a lack of active adsorption sites. The more metal ions in solution, the more active sites were occupied, reducing further adsorption (Gao et al. 2009). Cu (II) adsorption by bauxite was found to be a little higher than by montmorillonite for initial concentrations of 24–102 mg L^{-1} (Fig. 3). However, Zn adsorption on bauxite was higher for values below 41 mg L^{-1}, while it was less than the adsorption on montmorillonite above that (Fig. 4).

High adsorption rates for Cu (II) and Zn (II) were achieved on both of the studied adsorbents. Maximum Cu and Zn adsorption was 99.65 and 99.41% on bauxite and 98.67 and 98.55% on montmorillonite, respectively. Montmorillonite and bauxite can be proposed as low cost sorbents for Cu and Zn removal from wastewater and as alternative adsorptive barriers for contaminated areas. Some reactive media remove contaminants by physical contact while others work by altering the bio-geochemical processes in the treatment zone, thus providing conditions conducive for contaminant immobilization or (bio) degradation (Shabalala et al. 2017).

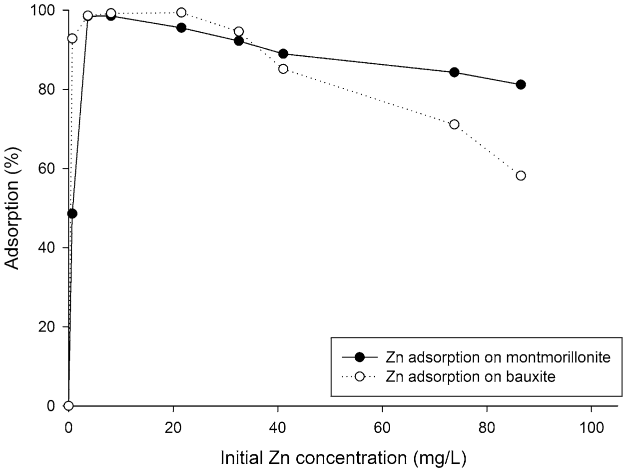

Fig. 4 Effect of initial Zn concentration on the adsorption rate

The effect of pH was studied over a range of 2–13 while maintaining the other parameters constant. Figure 5 shows that the sorption capacity of both Cu and Zn on both adsorbents generally increased with pH. Eloussaief et al. (2009) also confirmed that the initial solution pH is a key adsorption parameter that strongly affects metal adsorption because of the decreased positive charges on the adsorbent surface with an increased pH. The pH of the solution also affects the adsorption of metal ions because it affects the solubility and species of the metal ions, the concentration of counter ions on the functional groups of the adsorbents, and the degree of ionization of the adsorbate (Huang et al. 2014; Pavasant et al. 2006). Sdiri et al. (2014) indicated that the sorption of metal ions was also suppressed in an

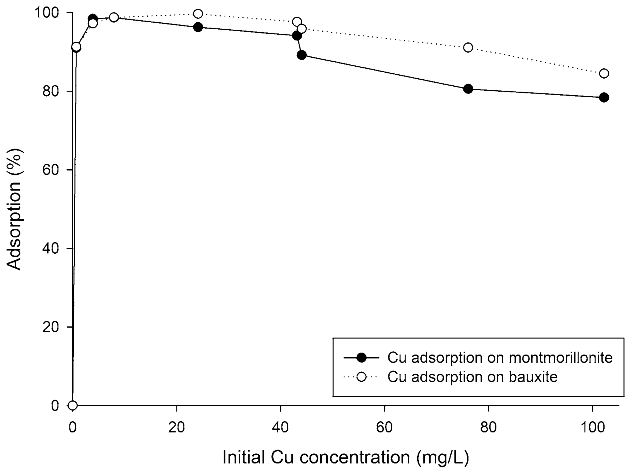

Fig. 3 Effect of initial Cu concentration on the adsorption rate

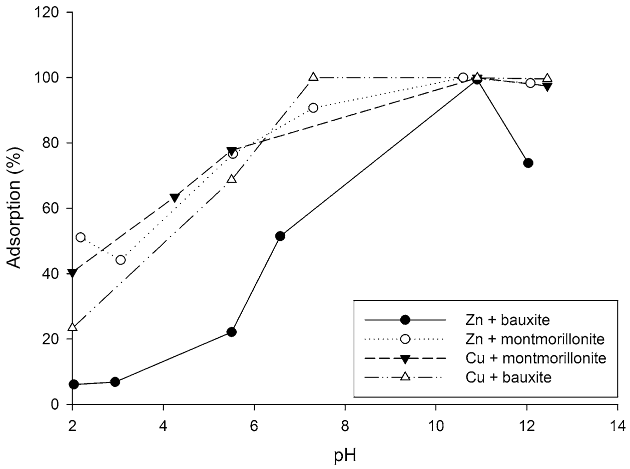

Fig. 5 Effect of equilibrium m pH on the adsorption of Cu and Zn on montmorillonite and bauxite

acidic environment (pH < 4) by the greater presence of H^+, which competes for the available reactive sites. The adsorption of Zn on bauxite decreased from >90 to ≈70% as the pH increased from 11 to 12. Each metal ion has an optimum pH range for adsorption, which depends on the type of adsorbent, solubility of constituents, and the type of adsorbed ions. It all depends on the zeta potential.

Combined use of reactive organic and inorganic materials in a PB may be beneficial in terms of providing alkalinity/buffering of pH and activation of additional removal mechanisms (e.g. precipitation, co-precipitation, and/or sorption). Organic materials may include agricultural by-products, sewage sludge, and organic wastes (Komnitsas et al. 2013).

An isothermal test was used to evaluate the adsorptive capacity of the bauxite and montmorillonite to uptake metal ions from an aqueous solution. The Freundlich and Langmuir equations were used to describe the experimental data. In order to optimize the design of an adsorption system, it is important to establish the most appropriate correlations of the equilibrium data of each system. The parameters obtained from the different models provide important information on the adsorption mechanisms, the surface properties, and affinities of the adsorbent (Malarvizhi and Santhi 2013). The Freundlich and Langmuir adsorption constants are given in Table 2. Copper and zinc adsorption isotherms fitted well with both the Freundlich and Langmuir models. Freundlich and Langmuir correlation coefficients ranged from 0.96 to 0.98 and 0.95 to 0.99, respectively. Smaller values of $1/n_f$ (<1) indicates that the adsorbent surface was heterogeneous. The maximum adsorption was found for Cu on bauxite, with a K_f value of 4.179 L g^{-1}; the maximum adsorbed capacity, Q_o, calculated from the Langmuir model, reached 9.115 mg g^{-1}. The adsorption capacity of the montmorillonite was higher for Cu than for Zn with K_f and Q_o values of 1.978 and 8.136, respectively. The Langmuir maximum adsorption capacities (C_s) of other natural clays (Musso et al. 2014) for Cu(II) and Zn(II) are given in Table 3. Generally, positively charged ions are attracted to negatively charged sites on the clay particles. The negatively charged sites on the montmorillonite make it an efficient adsorbent for cationic species such as Cu and Zn (Zhaoa and He 2014).

Table 3 Maximum adsorption capacities of various natural clays for Cu and Zn adsorption

Adsorbent	Cu (II) (mg/g)	Zn (II) (mg/g)
Natural bentonite (30 °C, pH 6.76)	–	68.49
Raw bentonite (25 °C, pH 6.5)	–	73.50
Na-montmorillonite	132.9	–
Calcareous clays	27.39–17.88	22.72–15.60
Raw bentonite	32.17	–
Na-bentonite (22 °C, pH 5 for Cu; 6 for Zn)	30	23.1
Natural bentonite (20 °C, pH 4.5)	–	52.91

However, bauxite showed a higher affinity than montmorillonite for both metals. Two characteristics of bauxite contribute to its high adsorption potential: its alkalinity, which favours hydrolysis and precipitation of metals as hydroxides and carbonates, and the large concentration of iron and aluminium (including hydroxides and oxyhydroxides), which provide surface sites for sorption reactions by metals (Klauber et al. 2009). Lombi et al. (2002) found that bauxite residues from Hungary effectively immobilized Cu and Zn in soil pore waters, lowering metal concentrations.

Conclusions

Cu (II) adsorption on the studied adsorbents was higher than Zn (II). Each metal ion can have different adsorption rates on various adsorbents. Adsorption capability of many other specific raw materials can be investigated.

Table 2 Freundlich and Langmuir constants for Cu and Zn adsorption on bauxite and montmorillonite

Isotherms	Isotherm constants	Cu on bauxite	Cu on montmorillonite	Zn on bauxite	Zn on montmorillonite
Freundlich isotherm	K_f (L g^{-1})	4.179	1.978	2.882	1.868
	$1/n_f$	0.244	0.479	0.161	0.491
	n_f (non-dimensional)	4.098	2.088	6.230	2.037
	R^2	0.97	0.96	0.96	0.98
Langmuir isotherm	$1/Q_o \times b$ (g L^{-1})	0.145	0.305	0.176	0.336
	$1/Q_o$ (g mg^{-1})	0.110	0.123	0.192	0.130
	b (L mg^{-1})	0.757	0.402	1.095	0.386
	Q_o (mg g^{-1})	9.115	8.136	5.197	4.290
	R^2	0.98	0.96	0.99	0.95

Bauxite showed a greater adsorption capacity than the montmorillonite for the studied metals. However, both raw materials have the potential to be effectively used as low cost sorbents for Cu and Zn removal from wastewaters. This ability can also be researched as treatment technologies since these materials are abundant and locally available.

The high adsorption capacity of montmorillonite is due to its negatively charged sites and their strong retention of metal ions, while the alkalinity and high concentrations of iron (18.27%) and aluminum oxides (53.82%) are likely responsible for the high metal adsorption potential of the bauxite. Both the montmorillonite and bauxite can possibly be used in alternative adsorptive barriers for fields contaminated with Cu and Zn, and likely other metals.

Both of the studied adsorbents can be used as amendments to improve the properties of the soils at old mining areas to prevent metal leaching to groundwater or to isolate urban waste leachate. In addition, pH was found to be an important parameter that strongly affects metal precipitation and metal adsorption in soil. Adsorption of Cu (II) and Zn (II) on the studied materials was high at pH values of 8 and above. Therefore, pH adjustments (such as lime application) in contaminated fields may be effective as a contamination management technique.

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